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**Ogawa et al.**

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(54) **NONAQUEOUS ELECTROLYTE BATTERY USING POLYACID AND/OR POLYACID COMPOUND**

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(51) **Int. Cl.**

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**H01M 10/0567** (2010.01)  
**H01M 10/0568** (2010.01)  
**H01M 10/0569** (2010.01)

(52) **U.S. Cl.**

CPC ..... **H01M 10/0567** (2013.01); **H01M 10/0568** (2013.01); **H01M 10/0569** (2013.01)  
USPC ..... **429/215**; 429/188; 429/218.1; 429/212

(58) **Field of Classification Search**

CPC ..... H01M 10/0567; H01M 10/0568; H01M 10/0569  
USPC ..... 429/188, 218.1, 212, 215  
See application file for complete search history.

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(57) **ABSTRACT**

A nonaqueous electrolyte battery includes: a positive electrode having a positive electrode active material layer that includes a positive electrode active material, a binder, and a compound having a pyrrolidone skeleton; a negative electrode having a negative electrode active material layer; a nonaqueous electrolyte that includes a solvent and an electrolyte salt; and a polyacid and/or a polyacid compound contained inside the battery.

**10 Claims, 10 Drawing Sheets**

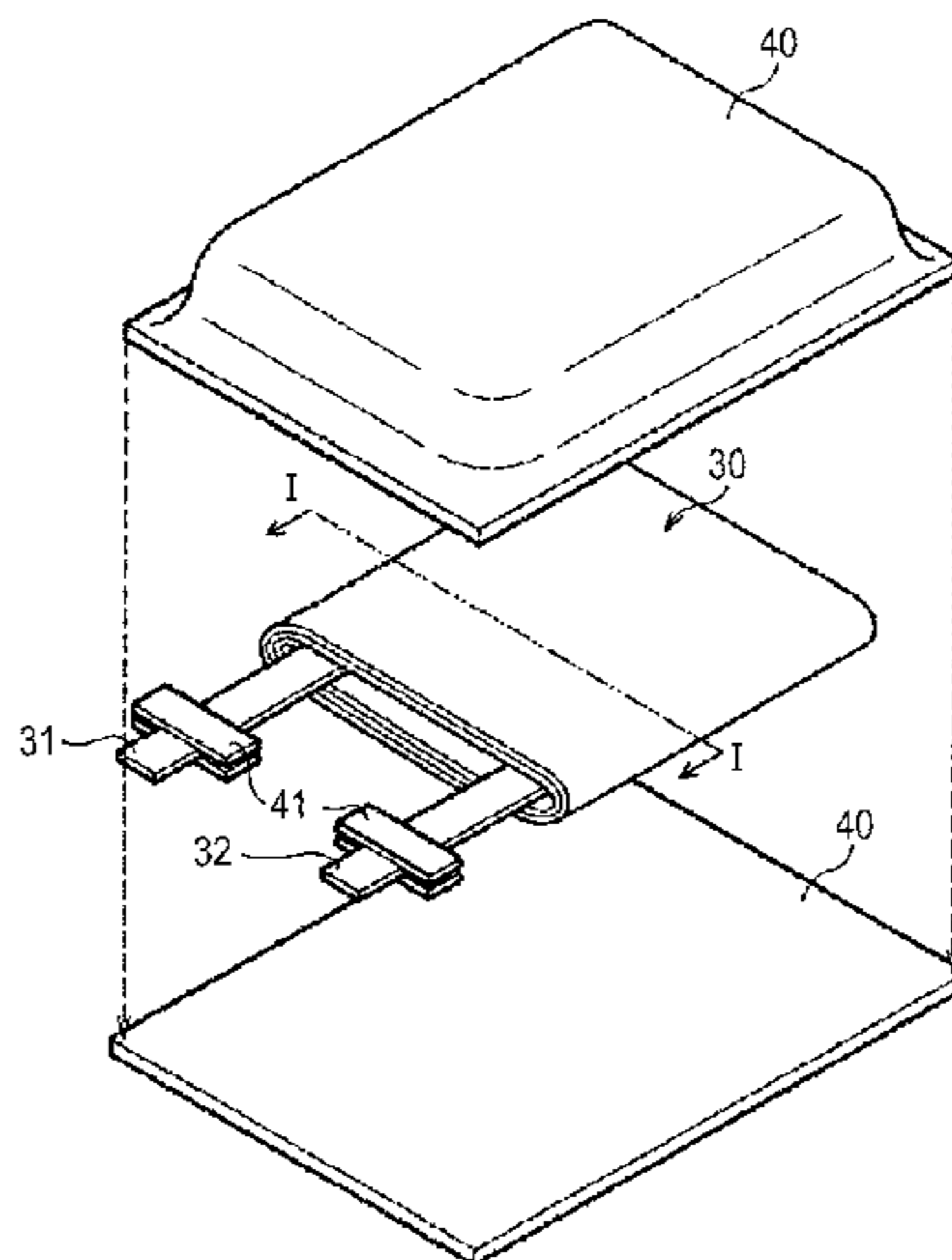


FIG. 1

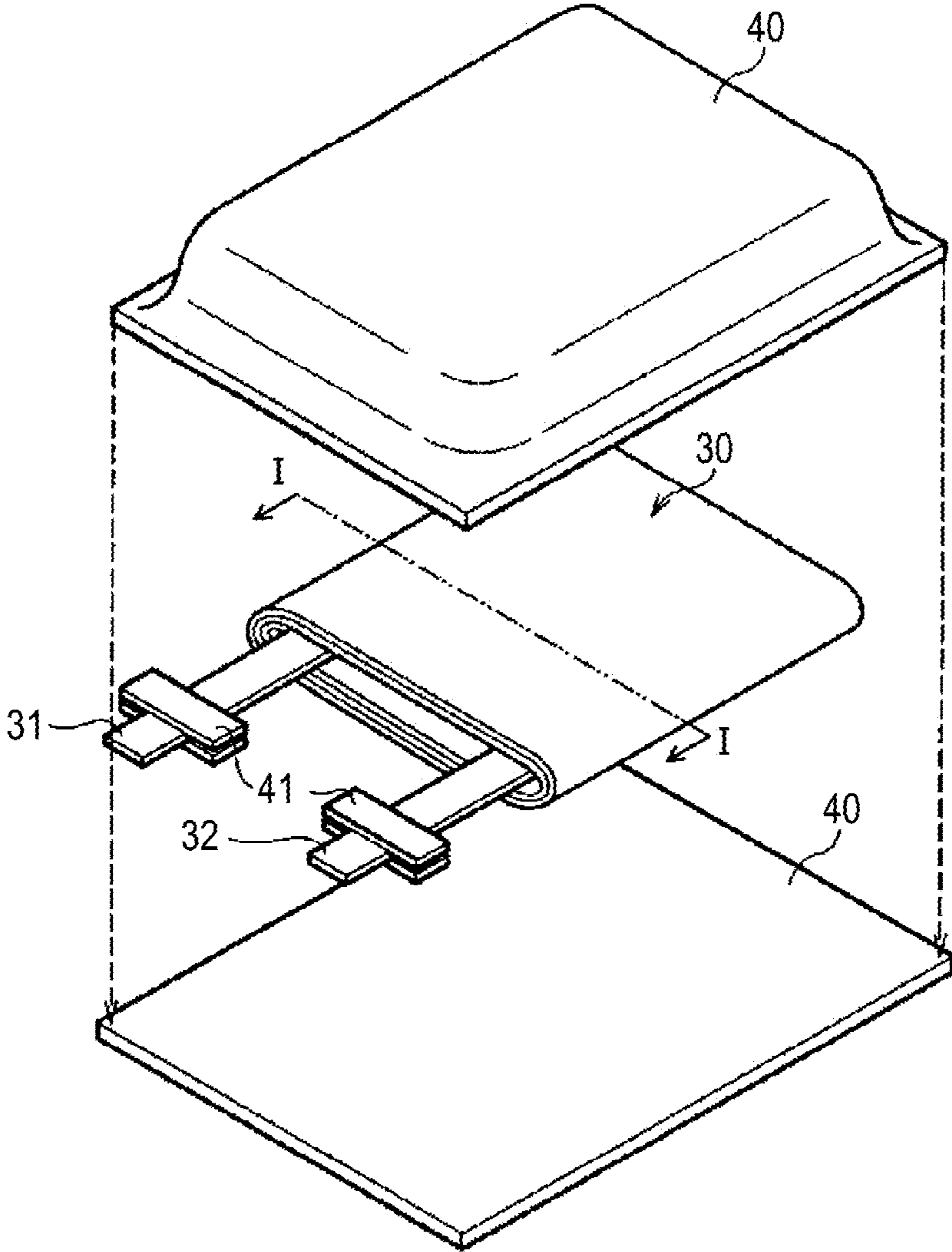


FIG. 2

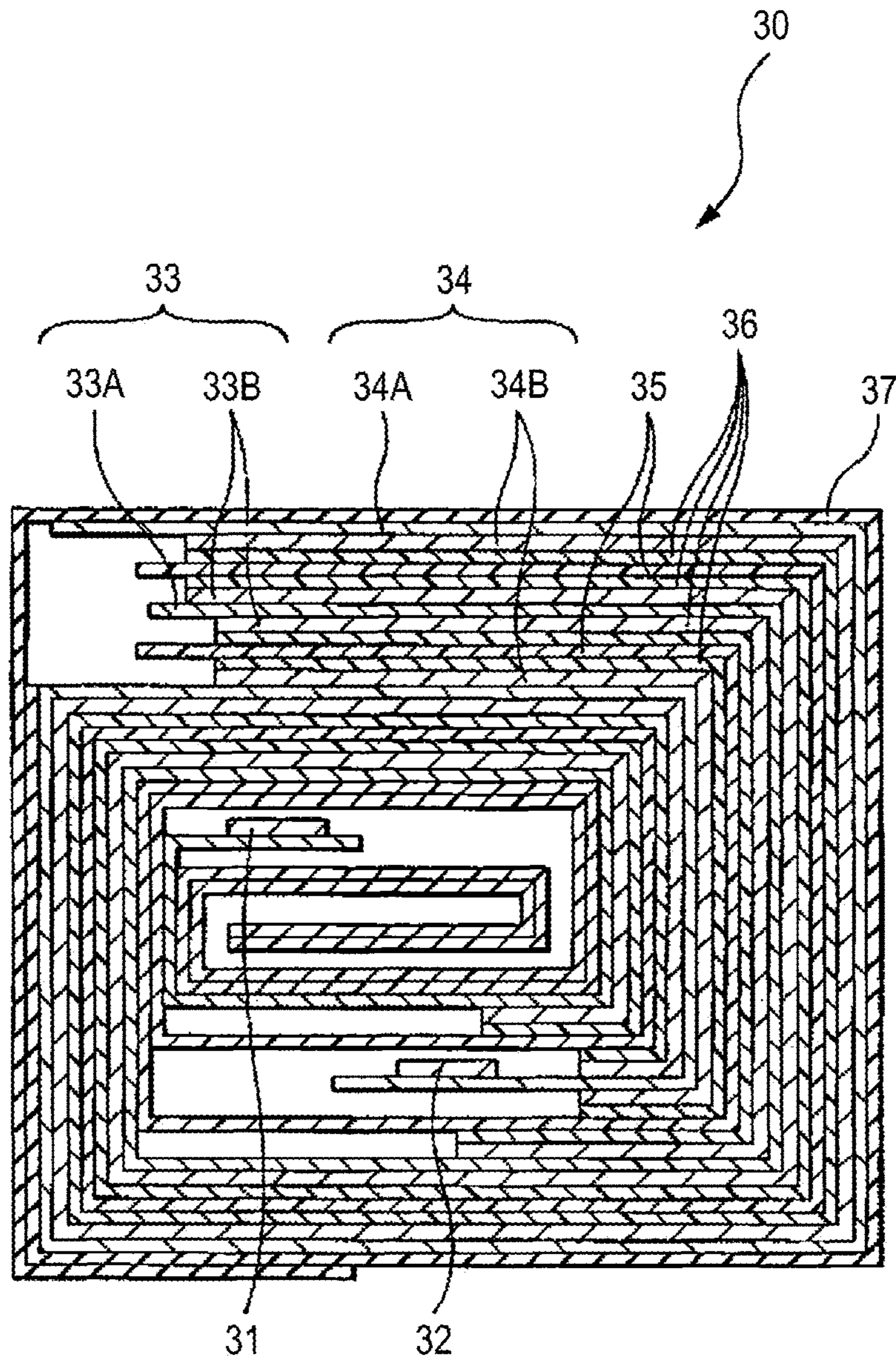


FIG. 3

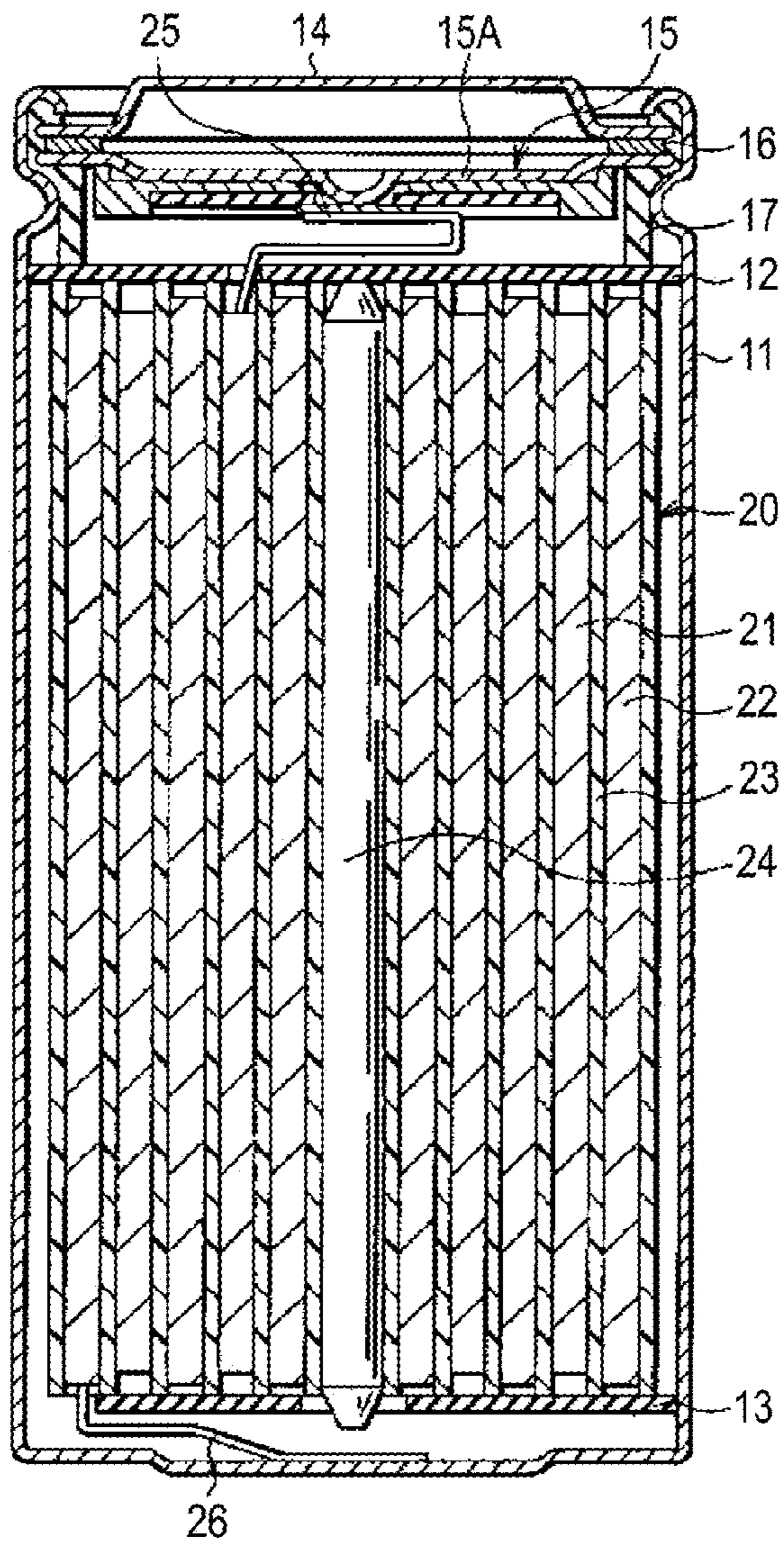


FIG. 4

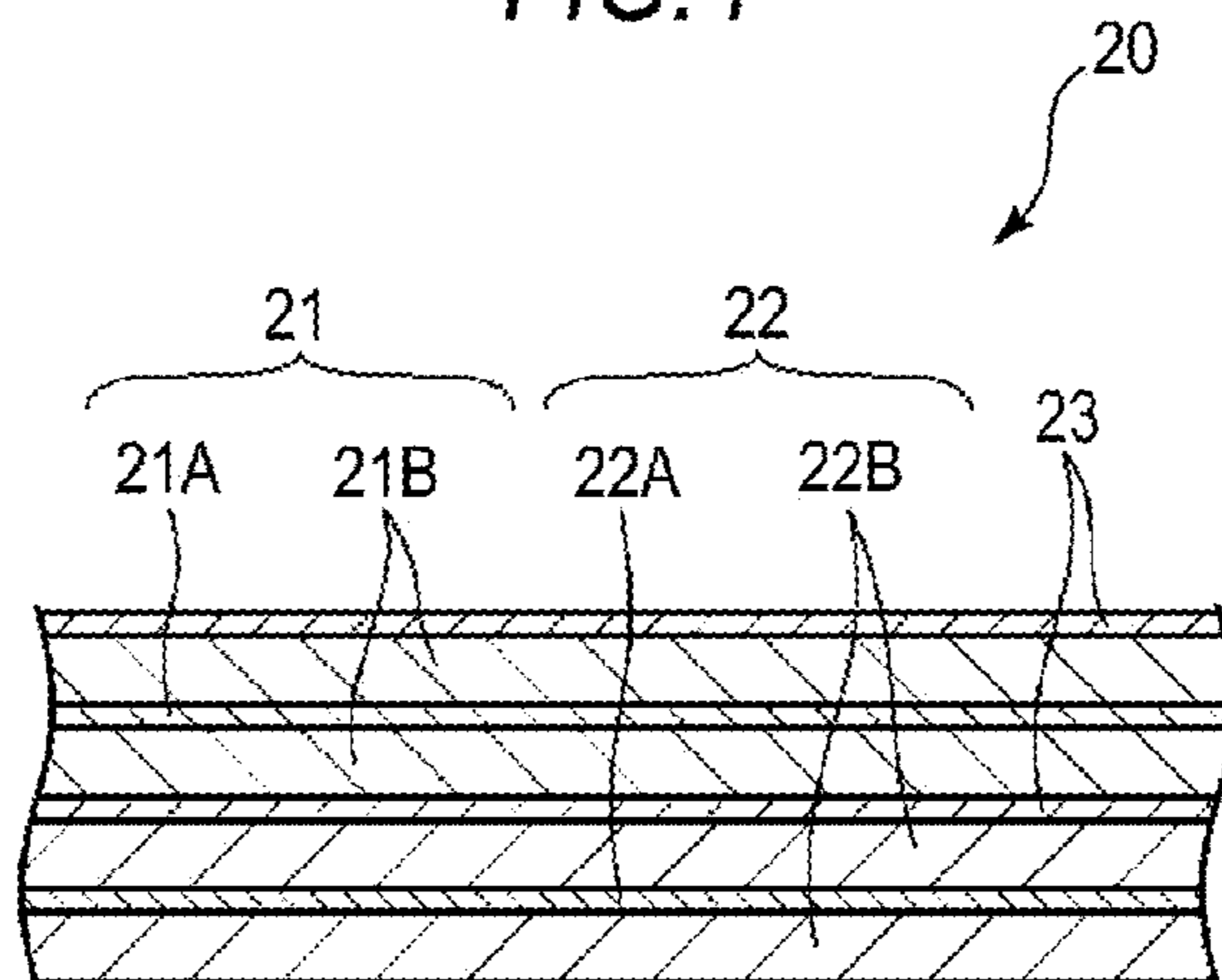


FIG. 5

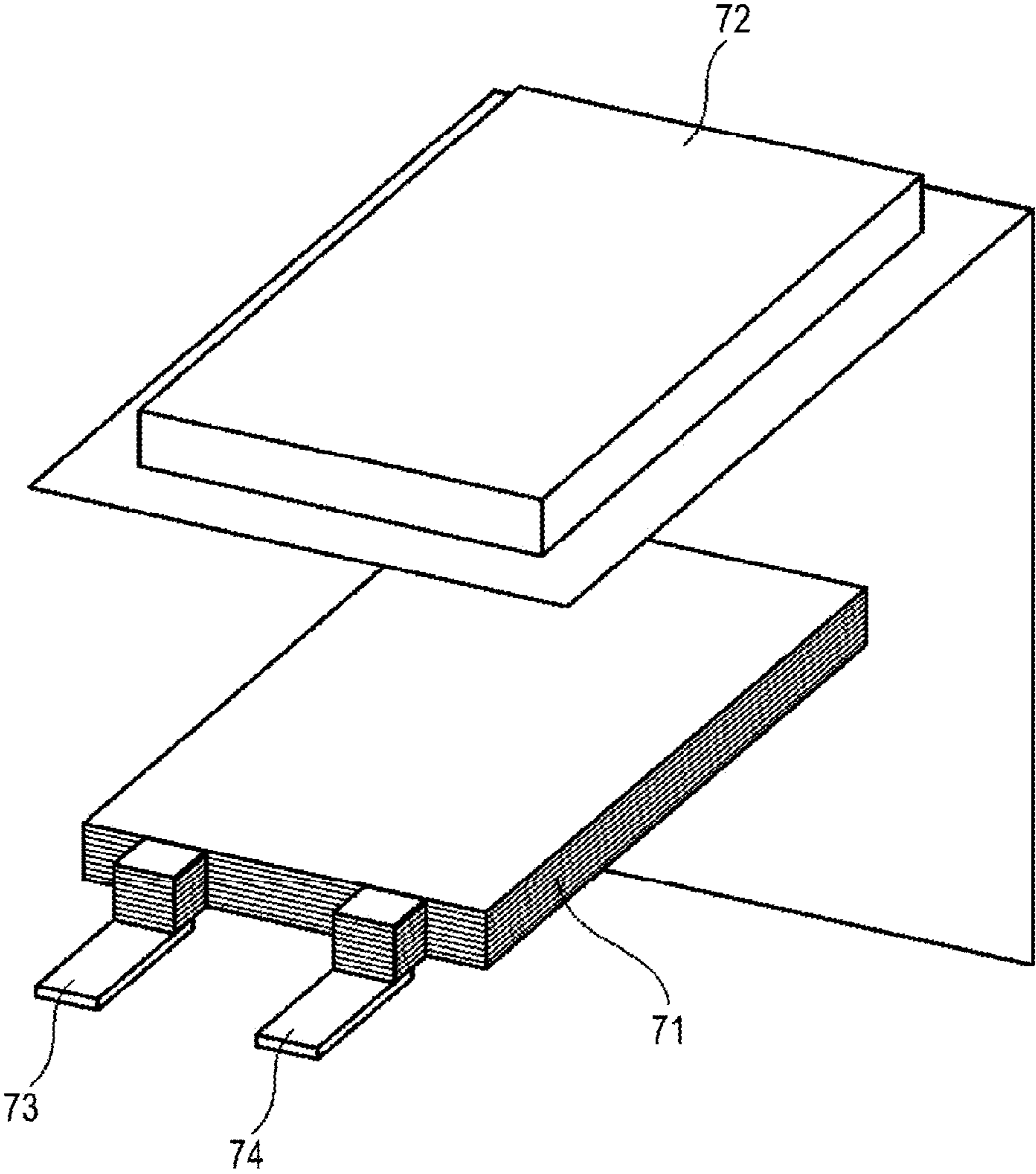


FIG. 6

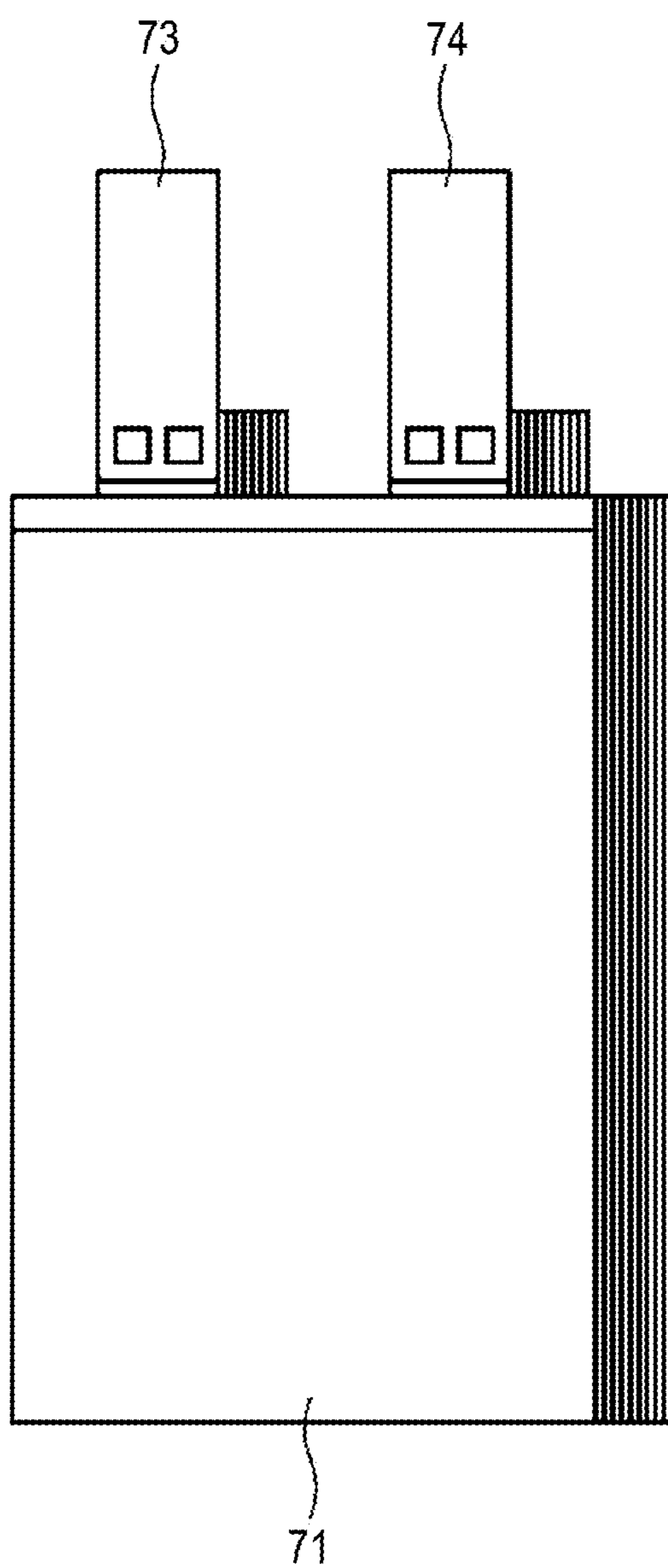


FIG. 7

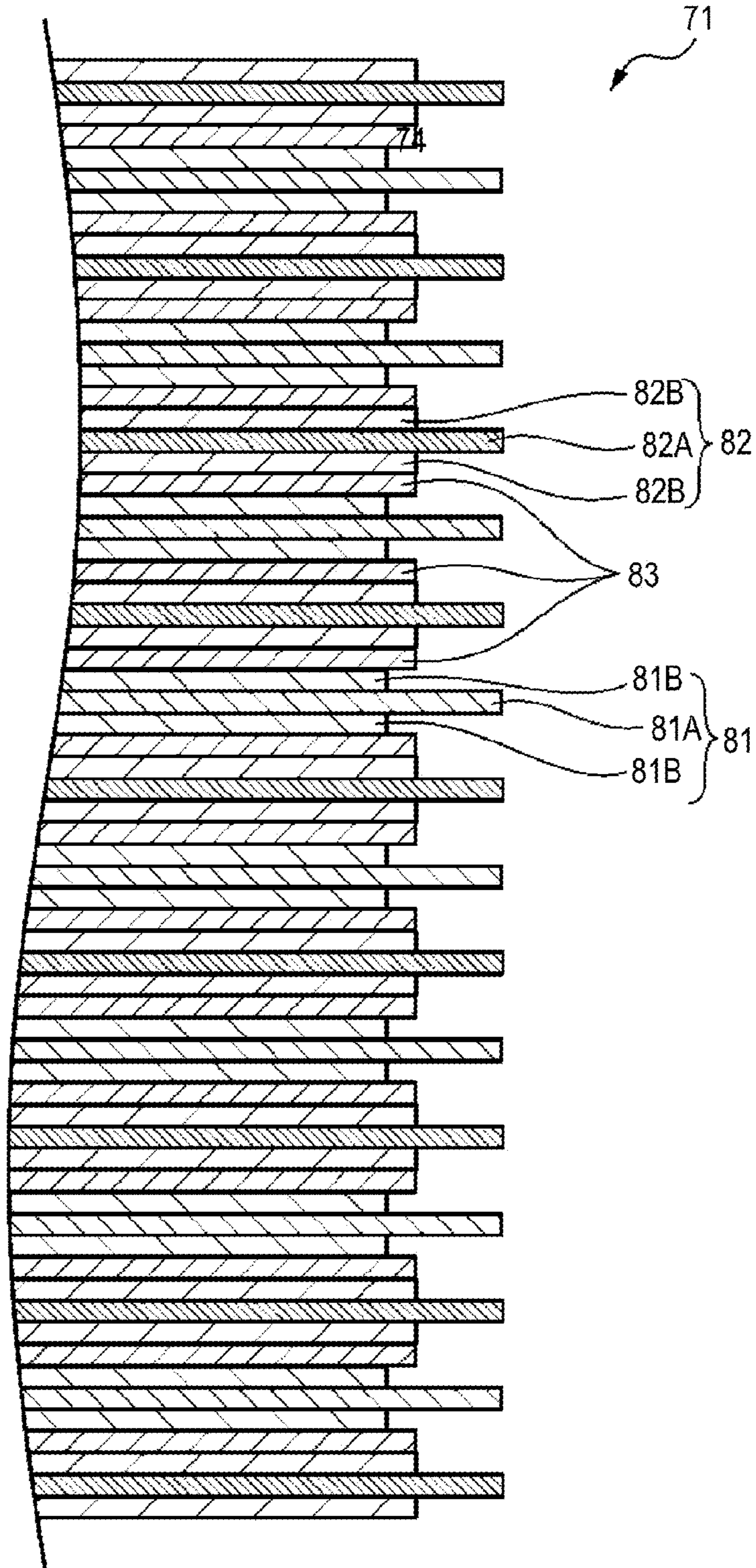


FIG. 8

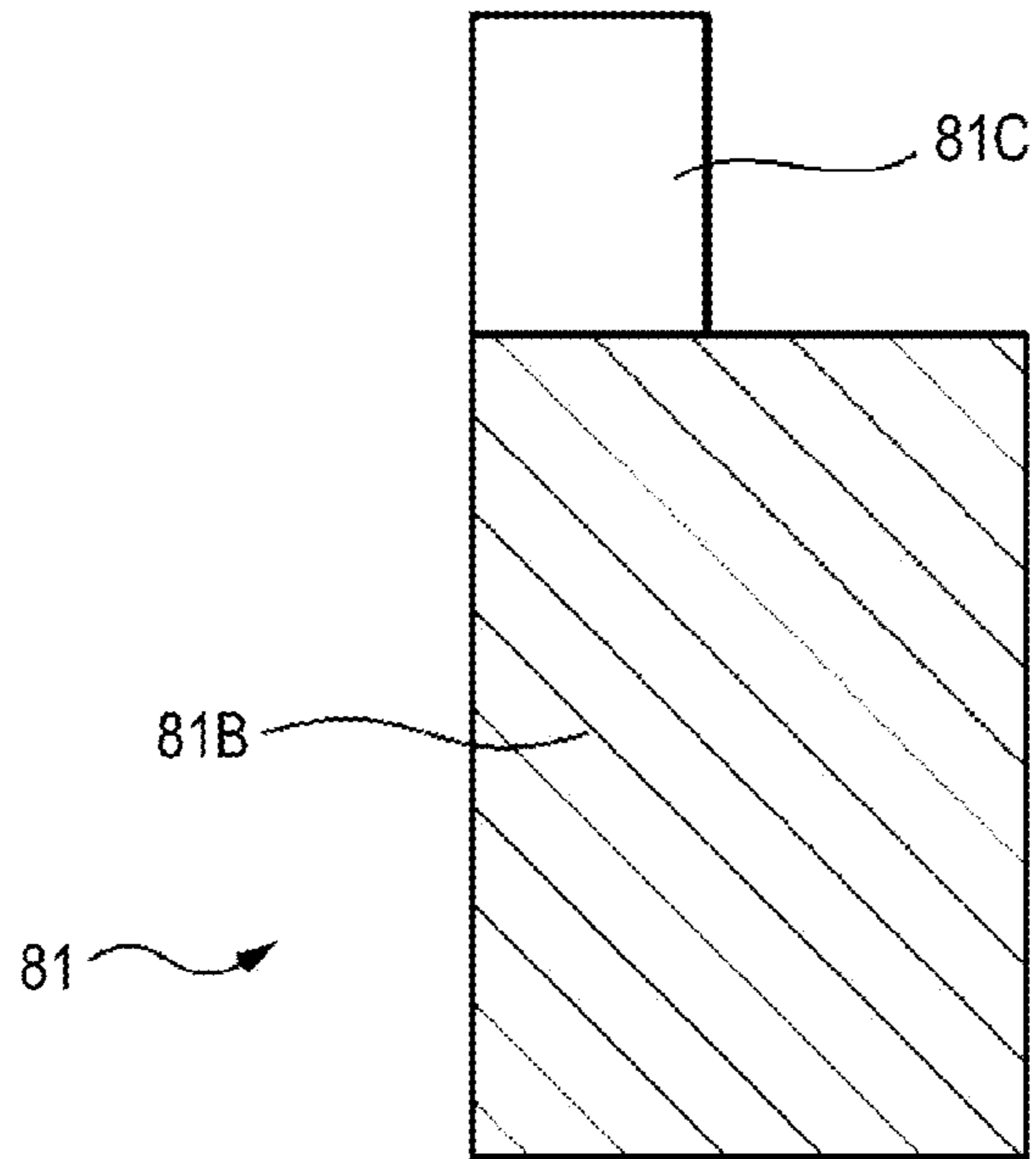
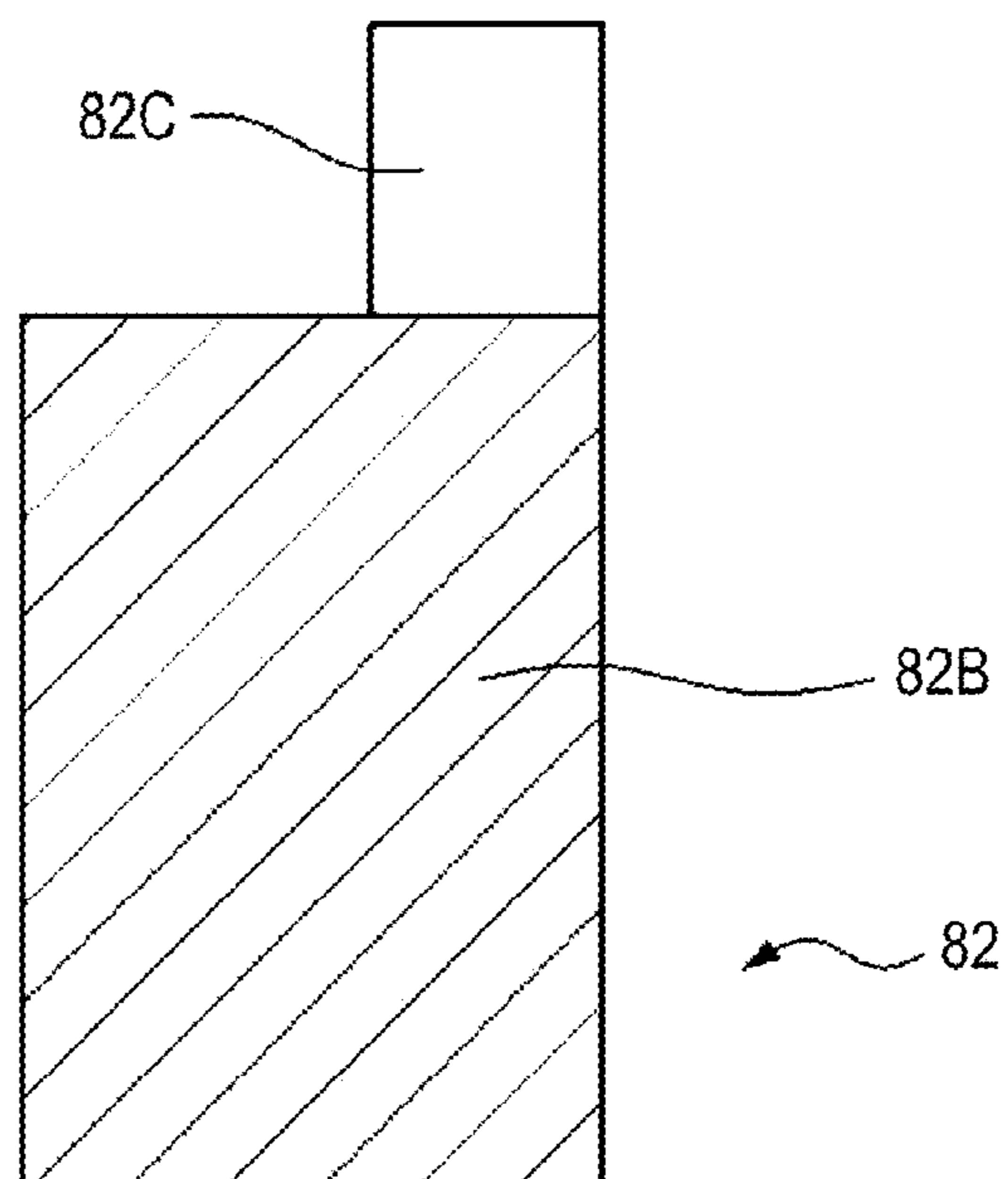
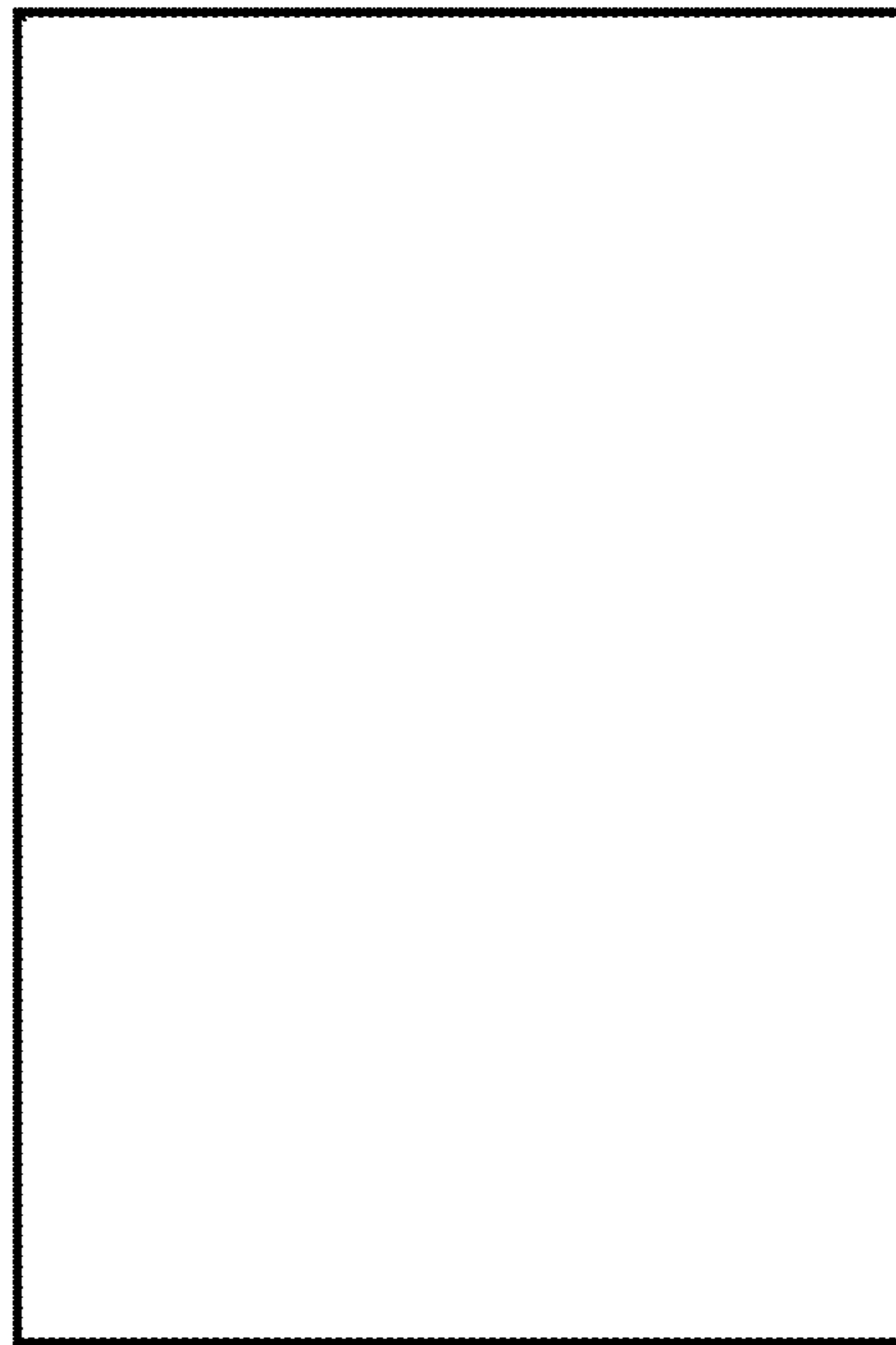


FIG. 9





*FIG. 10*



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FIG. 11

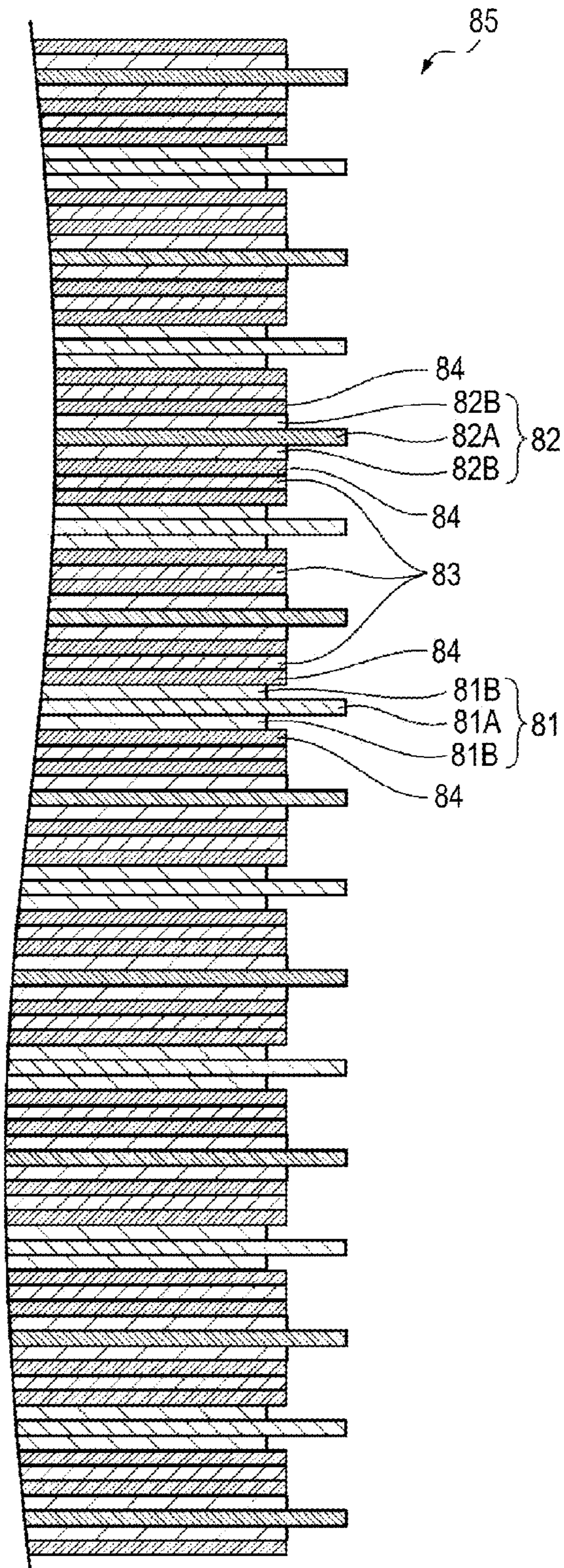
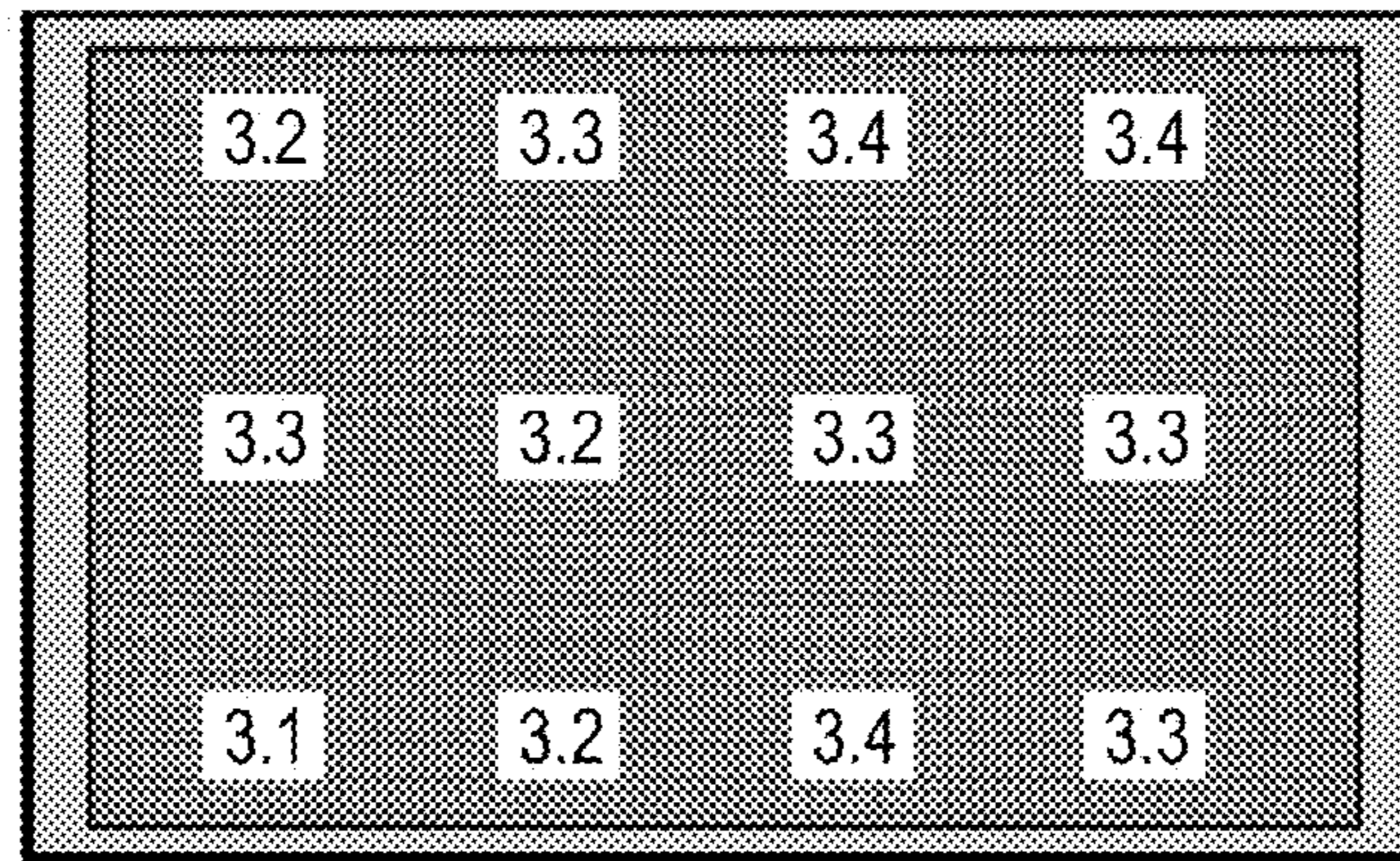


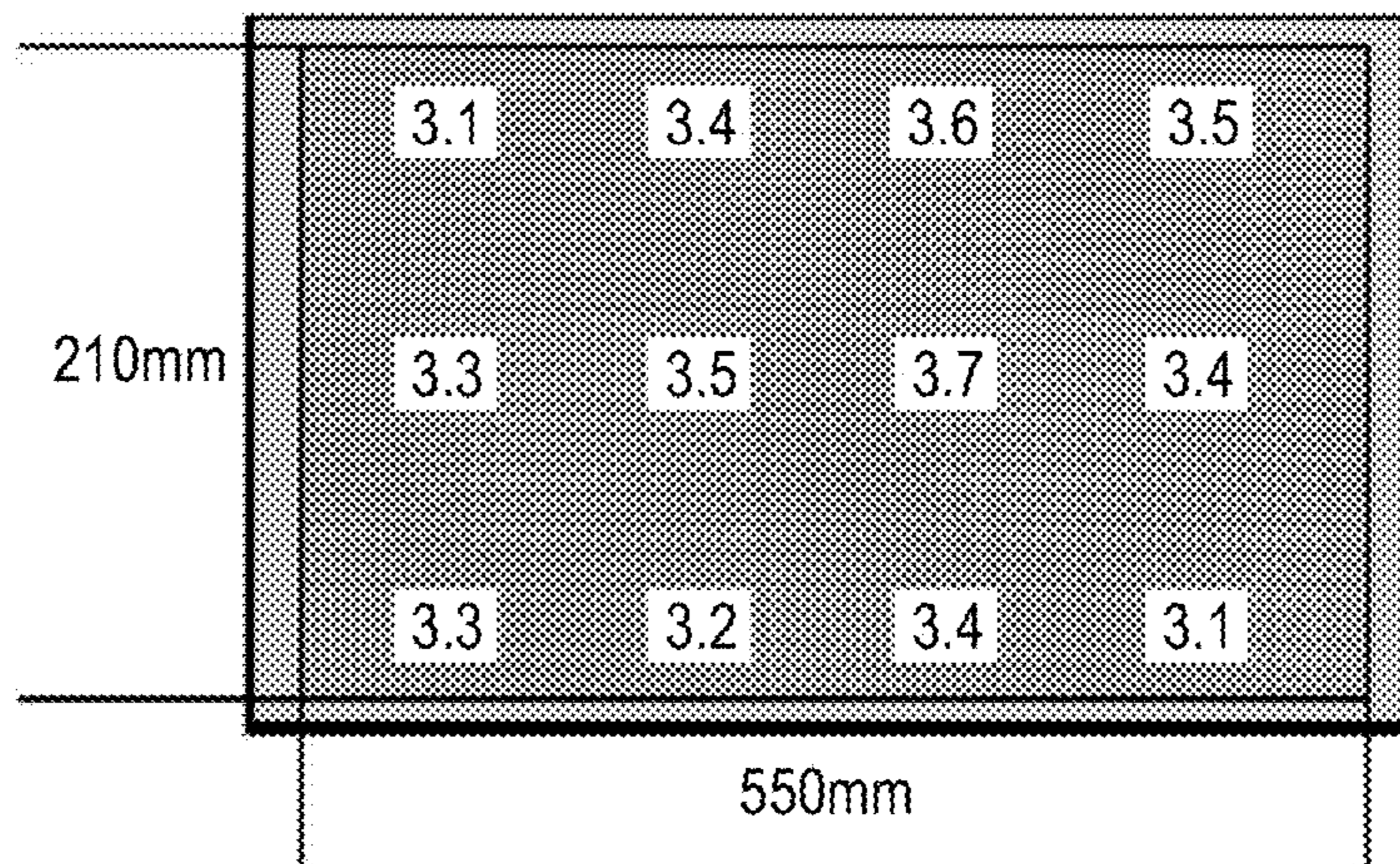
FIG. 12

TEST EXAMPLE 1-1



AVERAGE 3.28 [ $\Omega$ ]  
STANDARD DEVIATION 0.094

TEST EXAMPLE 1-2



AVERAGE 3.38 [ $\Omega$ ]  
STANDARD DEVIATION 0.186

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**NONAQUEOUS ELECTROLYTE BATTERY  
USING POLYACID AND/OR POLYACID  
COMPOUND**

CROSS REFERENCES TO RELATED  
APPLICATIONS

The present application claims priority to Japanese Priority Patent Application JP 2010-044807 filed in the Japan Patent Office on Mar. 2, 2010, the entire contents of which is hereby incorporated by reference.

BACKGROUND

This application relates to nonaqueous electrolyte batteries, specifically to nonaqueous electrolyte batteries that use a nonaqueous electrolyte containing an organic solvent and an electrolyte salt.

Efforts have been made to reduce the size and weight of portable electronic devices such as camera-integrated VCRs, digital still cameras, cell phones, personal digital assistants, and laptop computers. In this connection, there has been active research and development to improve the energy density of batteries, particularly secondary batteries, used as the portable power source of such electronic devices.

Lithium ion secondary batteries that use carbon, a lithium-transition metal composite oxide, and a carbonate ester mixture for the negative electrode active material, the positive electrode active material, and the electrolytic solution, respectively, have been put to a wide range of practical applications for their ability to provide greater energy density than other nonaqueous electrolytic solution secondary batteries such as lead batteries and nickel cadmium batteries.

Laminated lithium ion secondary batteries that use an aluminum laminate film for the exterior particularly have high energy density because of lightness. Laminated polymer lithium ion secondary batteries also have widespread use among the laminated lithium ion secondary batteries, because the polymer used for the battery swells with the electrolytic solution, and suppresses deformation of the laminated battery.

JP-A-2003-331847 describes a battery that includes at least one carbon material having an average primary particle diameter of 10 to 100 nm, a binder such as polyvinylidene fluoride, and a vinylidene fluoride-hexafluoropropane copolymer, and a compound having a pyrrolidone skeleton, and in which the electrode blackness is 1.20 or more.

JP-A-2009-004227 describes a nonaqueous electrolyte battery provided with a positive electrode mixture layer configured to include one or more positive electrode active materials of olivine crystal structure, polyvinylpyrrolidone (PVP), and, optionally, a conductive auxiliary agent such as graphite, and a binder such as polyvinylidene fluoride (PVdF).

SUMMARY

As the development of the recent electronic devices progresses in many areas including the movement towards higher performance of electronic components such as the CPU (central processing unit), there is a corresponding increase in the amount of heat generation, exposing the batteries to a high-temperature atmosphere. Capacity decrease that occurs in batteries exposed to a high-temperature atmosphere needs to be suppressed.

Accordingly, there is a need for a nonaqueous electrolyte battery in which capacity decrease during high-temperature storage can be suppressed.

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According to one embodiment, there is provided a nonaqueous electrolyte battery that includes:

a positive electrode having a positive electrode active material layer that includes a positive electrode active material, a binder, and a compound having a pyrrolidone skeleton;

a negative electrode having a negative electrode active material layer;

a nonaqueous electrolyte that includes a solvent and an electrolyte salt; and

a polyacid and/or a polyacid compound contained inside the battery.

According to another embodiment, there is provided a nonaqueous electrolyte battery that includes:

a positive electrode having a positive electrode active material layer that includes a positive electrode active material, a binder, and a compound having a pyrrolidone skeleton;

a negative electrode having a negative electrode active material layer;

a nonaqueous electrolyte that includes a solvent and an electrolyte salt; and

a coating that originates in a polyacid and/or a polyacid compound, and is formed on the positive electrode.

In the foregoing one embodiment, the compound that originates in the polyacid and/or polyacid compound added to the nonaqueous electrolyte battery deposits on the surface of the positive electrode and forms an inorganic coating. Because the positive electrode active material layer includes a compound having a pyrrolidone skeleton, the positive electrode active material layer has uniform conductivity. The uniform conductivity of the positive electrode active material layer promotes the inorganic coating that originates in the polyacid and/or polyacid compound to be evenly formed on the surface of the positive electrode. In this way, deterioration of the electrode under a high-temperature environment, and thus capacity decrease of the battery can be suppressed.

In the foregoing another embodiment, the positive electrode active material layer includes a compound having a pyrrolidone skeleton, and thus has uniform conductivity. The uniform conductivity of the positive electrode active material layer allows the inorganic coating that originates in the polyacid and/or polyacid compound to be evenly formed on the surface of the positive electrode. In this way, deterioration of the electrode under a high-temperature environment, and thus capacity decrease of the battery can be suppressed.

With the embodiments of the present application, capacity decrease during high-temperature storage can be suppressed.

Additional features and advantages are described herein, and will be apparent from the following Detailed Description and the figures.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is an exploded perspective view illustrating an exemplary configuration of a nonaqueous electrolyte battery according to an embodiment.

FIG. 2 is a cross sectional view of the wound electrode unit of FIG. 1 taken along the line I-I.

FIG. 3 is a cross sectional view illustrating an exemplary configuration of a nonaqueous electrolyte battery according to an embodiment.

FIG. 4 is an enlarged cross sectional view of a portion of the wound electrodes.

FIG. 5 is an exploded perspective view illustrating an exemplary configuration of a nonaqueous electrolyte battery according to an embodiment.

FIG. 6 is a perspective view illustrating an example of an external appearance of a battery element.

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FIG. 7 is a cross sectional view illustrating an exemplary configuration of the battery element.

FIG. 8 is a plan view illustrating an exemplary shape of a positive electrode.

FIG. 9 is a plan view illustrating an exemplary shape of a negative electrode.

FIG. 10 is a plan view illustrating an exemplary shape of a separator.

FIG. 11 is a cross sectional view illustrating an exemplary configuration of a battery element used in a nonaqueous electrolyte battery according to an embodiment.

FIG. 12 is a schematic diagram representing the measurement results of Test Examples 1-1 to 1-2.

### DETAILED DESCRIPTION

Embodiments of the present application will be described below in detail with reference to the drawings.

The following will describe embodiments of the present application referring to the accompanying drawings. Descriptions will be given in the following order.

1. First Embodiment (First example of nonaqueous electrolyte battery)

2. Second Embodiment (Second example of nonaqueous electrolyte battery)

3. Third Embodiment (Third example of nonaqueous electrolyte battery)

4. Fourth embodiment (Third example of nonaqueous electrolyte battery)

5. Fifth embodiment (Third example of nonaqueous electrolyte battery)

6. Other Embodiments (Variations)

1. First Embodiment

(Battery Configuration)

A nonaqueous electrolyte battery according to First Embodiment is described. FIG. 1 is an exploded perspective view representing a configuration of the nonaqueous electrolyte battery according to First Embodiment. FIG. 2 is a magnified cross sectional view of a wound electrode unit 30 of FIG. 1 at the line I-I.

The nonaqueous electrolyte battery is, for example, a chargeable and dischargeable nonaqueous electrolyte secondary battery, and basically structured to include a film-like exterior member 40, and a wound electrode unit 30 housed in the exterior member 40 with a positive electrode lead 31 and a negative electrode lead 32 attached to the wound electrode unit 30. The battery structure using the film-like exterior member 40 is called a laminate film structure.

For example, the positive electrode lead 31 and the negative electrode lead 32 lead out in the same direction out of the exterior member 40. The positive electrode lead 31 is formed using, for example, metallic material such as aluminum. The negative electrode lead 32 is formed using, for example, metallic material such as copper, nickel, and stainless steel. These metallic materials are formed into, for example, a thin plate or a mesh.

The exterior member 40 is formed using, for example, an aluminum laminate film that includes a nylon film, an aluminum foil, and a polyethylene film laminated in this order. For example, the exterior member 40 is structured from a pair of rectangular aluminum laminate films fused or bonded with an adhesive at the peripheries with the polyethylene films facing the wound electrode unit 30.

An adhesive film 41 that prevents entry of external air is inserted between the exterior member 40 and the positive and negative electrode leads 31 and 32. The adhesive film 41 is configured using a material that has adhesion to the positive

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electrode lead 31 and the negative electrode lead 32. Examples of such material include polyolefin resins such as polyethylene, polypropylene, modified-polyethylene, and modified-polypropylene.

The exterior member 40 may be configured from laminate films of other laminate structures, instead of the aluminum laminate film, or from a polypropylene or other polymer films, or metal films.

FIG. 2 is a cross section of the wound electrode unit 30 of FIG. 1, taken along the line I-I. The wound electrode unit 30 is a wound unit of a positive electrode 33 and a negative electrode 34 laminated via a separator 35 and an electrolyte 36. The outermost periphery of the wound electrode unit 30 is protected by a protective tape 37.

(Positive Electrode)

The positive electrode 33 is structured from, for example, a positive electrode active material layer 33B provided on the both sides of a double-sided positive electrode collector 33A.

The positive electrode active material layer 33B may be provided only on one side of the positive electrode collector 33A.

The positive electrode collector 33A is configured using, for example, metallic material such as aluminum, nickel, and stainless steel.

The positive electrode active material layer 33B includes positive electrode active material, which is one or more positive electrode materials capable of storing and releasing lithium, and a compound having a pyrrolidone skeleton. Other materials such as a binder and a conductive agent also may be contained, as required.

(Positive Electrode Material)

Preferred examples of positive electrode material that can store and release lithium include: lithium composite oxides such as lithium cobalt oxide, lithium nickel oxide, solid solutions of these {for example,  $\text{Li}(\text{Ni}_x\text{CO}_y\text{Mn}_z)\text{O}_2$  ( $x$ ,  $y$ , and  $z$  satisfy  $0 < x < 1$ ,  $0 < y < 1$ ,  $0 \leq z < 1$ ,  $x + y + z = 1$ ),  $\text{Li}(\text{Ni}_x\text{CO}_y\text{Al}_z)\text{O}_2$  ( $x$ ,  $y$ , and  $z$  satisfy  $0 < x < 1$ ,  $0 < y < 1$ ,  $0 \leq z < 1$ ,  $x + y + z = 1$ )}, spinel manganese ( $\text{LiMn}_2\text{O}_4$ ), and solid solutions of these { $\text{Li}(\text{Mn}_{2-v}\text{Ni}_v)\text{O}_4$  ( $v < 2$ )}; and phosphoric acid compounds of an olivine structure, such as lithium iron phosphate ( $\text{LiFePO}_4$ ), and  $\text{Li}_x\text{Fe}_{1-y}\text{M}_2\text{PO}_4$  (where  $\text{M}_2$  represents at least one selected from manganese (Mn), nickel (Ni), cobalt (Co), zinc (Zn), and magnesium (Mg), and  $0.9 \leq x \leq 1.1$ ). These are preferable for their ability to produce high energy density.

Particularly preferred as the positive electrode material capable of storing and releasing lithium, in terms of realizing higher capacity, is a high-nickel-content lithium nickel composite oxide represented by  $\text{LiNi}_x\text{M}_{1-x}\text{O}_2$  (where  $\text{M}$  is at least one element selected from groups 2 to 15 excluding Ni, and  $0.5 \leq x \leq 1.0$ ).

A positive electrode material produced by the coating treatment of lithium cobalt oxide, lithium nickel oxide, or solid solutions of these may be used as the positive electrode active material. Specifically, for example, a positive electrode material produced by coating at least part of the particle surfaces of lithium cobalt oxide, lithium nickel oxide, or solid solutions of these with phosphoric acid compounds such as lithium phosphate ( $\text{Li}_3\text{PO}_4$ ) and lithium iron phosphate ( $\text{LiFePO}_4$ ) may be used as the positive electrode active material. Swelling that might occur during high-temperature storage can be suppressed with the use of such positive electrode materials, because the lithium phosphate suppresses the electrolytic solution from contacting the lithium nickel composite oxide, and allows for conduction of only lithium ions. The coating treatment is performed by, for example, mixing the phosphoric acid compound with lithium cobalt oxide, lithium nickel oxide, or solid solutions of these using a ball milling machine.

Other examples of positive electrode material that can store and release lithium include: oxides such as titanium oxide, vanadium oxide, and manganese dioxide; disulfides such as iron disulfide, titanium disulfide, and molybdenum sulfide; sulfur; and conductive polymers such as polyaniline and polythiophene.

The positive electrode material that can store and release lithium may be other than these examples.

(Compound having a Pyrrolidone Skeleton)

Examples of the compound having a pyrrolidone skeleton include polyvinylpyrrolidone (PVP), and polypropylpyrrolidone. Preferably, polyvinylpyrrolidone (PVP) having a weight-average molecular weight of, for example, from 1,000 to 1,200,000, inclusive, is used. The weight-average molecular weight can be measured using a GPC (Gel Permeation Chromatography) method.

Examples of the binder include synthetic rubbers such as styrenebutadiene rubber, fluorine rubber, and ethylene propylene diene; and polymer materials such as polyvinylidene fluoride. These may be used alone or as a mixture of one or more. Of these, polyvinylidene fluoride is preferable. Polyvinylidene fluoride assumes a three-dimensional mesh structure in the positive electrode active material layer 33B, and, because the polyvinylpyrrolidone (PVP) is considered to reside along the three-dimensional mesh structure of the polyvinylidene fluoride, polyvinylidene fluoride allows the polyvinylpyrrolidone (PVP) to exhibit its effects without lowering ion permeability.

Examples of the conductive agent include carbon materials such as graphite and carbon black. These may be used alone or as a mixture of one or more.

(Negative Electrode)

The negative electrode 34 is structured to include, for example, a negative electrode active material layer 34B provided on the both sides of a double-sided negative electrode collector 34A. The negative electrode active material layer 34B may be provided only on one side of the negative electrode collector 34A.

The negative electrode collector 34A is configured using, for example, metallic material such as copper, nickel, and stainless steel.

The negative electrode active material layer 34B includes a negative electrode active material, which may be one or more negative electrode materials capable of storing and releasing lithium. Other materials such as a binder and a conductive agent also may be contained, as required. The same binder and conductive agent described in conjunction with the positive electrode can be used.

The negative electrode material that can store and release lithium may be, for example, carbon material. Examples of carbon material include easily graphitizable carbon, non-graphitizable carbon having a (002) plane distance of 0.37 nm or more, and graphite having a (002) plane distance of 0.34 nm or less. Specific examples include pyrolyzed carbons, cokes, glass-like carbon fibers, organic polymer compound calcined products, activated carbons, and carbon blacks. Cokes include pitch cokes, needle cokes, and petroleum cokes. The organic polymer compound calcined products refer to carbonized products obtained by calcining phenol resin, furan resin, or the like at appropriate temperatures. Carbon materials are preferred because they undergo a very few changes in crystal structure in the storage and release of lithium, and thus provide high energy density and excellent cycle characteristics, in addition to serving as conductive agents. The carbon material may be fibrous, spherical, granular, or scale-like in shape.

Aside from the carbon material, the negative electrode material that can store and release lithium may be, for example, material that, in addition to being capable of storing and releasing lithium, includes at least one of a metallic element and a semi-metallic element as the constituting element, because such materials also provide high energy density. Such negative electrode materials may include a metallic element or a semi-metallic element either alone or as an alloy or a compound, or may at least partially include one or more phases of these. As used herein, the "alloy" encompasses an alloy or two or more metallic elements, and an alloy of one or more metallic elements and one or more semi-metallic elements. Further, the "alloy" may include a non-metallic element. The composition may be a solid solution, a eutectic (eutectic mixture), or an intermetallic compound, or a mixture of two or more of these.

The metallic and semi-metallic elements are, for example, those capable of forming an alloy with lithium. Specific examples include magnesium (Mg), boron (B), aluminum (Al), gallium (Ga), indium (In), silicon (Si), germanium (Ge), tin (Sn), lead (Pb), bismuth (Bi), cadmium (Cd), silver (Ag), zinc (Zn), hafnium (Hf), zirconium (Zr), yttrium (Y), palladium (Pd), and platinum (Pt). At least one of silicon and tin is preferable, and silicon is more preferable, because these elements are highly capable of storing and releasing lithium, and can provide high energy density.

Examples of negative electrode material that includes at least one of silicon and tin include silicon, either alone or as an alloy or a compound, tin, either alone or as an alloy or a compound, and materials that at least partially include one or more phases of these.

Examples of silicon alloy include those including at least one non-silicon second constituting element selected from tin (Sn), nickel (Ni), copper (Cu), iron (Fe), cobalt (Co), manganese (Mn), zinc (Zn), indium (In), silver (Ag), titanium (Ti), germanium (Ge), bismuth (Bi), antimony (Sb), and chromium (Cr). Examples of tin alloy include those including at least one non-tin (Sn) second constituting element selected from silicon (Si), nickel (Ni), copper (Cu), iron (Fe), cobalt (Co), manganese (Mn), zinc (Zn), indium (In), silver (Ag), titanium (Ti), germanium (Ge), bismuth (Bi), antimony (Sb), and chromium (Cr).

Examples of tin compound and silicon compound include those containing, for example, oxygen (O) or carbon (C). The tin compound and the silicon compound may optionally include the second constituting elements exemplified above, in addition to tin (Sn) or silicon (Si).

Particularly preferred as the negative electrode material that includes at least one of silicon (Si) and tin (Sn) is, for example, a material that includes tin (Sn) as a first constituting element, and a second and a third constituting element in addition to first constituting element tin (Sn). The negative electrode material may be used together with the negative electrode materials exemplified above. The second constituting element is at least one selected from cobalt (Co), iron (Fe), magnesium (Mg), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), zirconium (Zr), niobium (Nb), molybdenum (Mo), silver (Ag), indium (In), cerium (Ce), hafnium (Hf), tantalum (Ta), tungsten (W), bismuth (Bi), and silicon (Si). The third constituting element is at least one selected from boron (B), carbon (C), aluminum (Al), and phosphorus (P). Inclusion of the second and third elements improves cycle characteristics.

A CoSnC-containing material is particularly preferable that includes tin (Sn), cobalt (Co), and carbon (C) as the constituting elements, and in which the carbon (C) content

ranges from 9.9 mass % to 29.7 mass %, inclusive, and in which the proportion of cobalt (Co) in the total of tin (Sn) and cobalt (Co) ( $\text{Co}/(\text{Sn}+\text{Co})$ ) ranges from 30 mass % to 70 mass %, inclusive. High energy density and excellent cycle characteristics can be obtained with these composition ranges.

The SnCoC-containing material may optionally include other constituting elements, as required. Preferred examples of other constituting elements include silicon (Si), iron (Fe), nickel (Ni), chromium (Cr), indium (In), niobium (Nb), germanium (Ge), titanium (Ti), molybdenum (Mo), aluminum (Al), phosphorus (P), gallium (Ga), and bismuth (Bi), which may be contained in combinations of two or more. Inclusion of these elements further improves capacity characteristics or cycle characteristics.

It is preferable that the SnCoC-containing material include a tin (Sn)-, cobalt (Co)-, and carbon (C)-containing phase, and that this phase have a low-crystalline or amorphous structure. Further, in the SnCoC-containing material, it is preferable that the constituting element carbon at least partially bind to the other constituting elements, namely, metallic elements or semi-metallic elements. Bonding of the carbon with other elements suppresses agglomeration or crystallization of tin (Sn) or other elements, which is considered to lower cycle characteristics.

The state of element binding can be measured by, for example, X-ray photoelectron spectroscopy (XPS). In XPS, the peak of the carbon 1s orbital (C1s) appears at 284.5 eV for graphite, when the device used is calibrated to provide a peak of the gold atom 4f orbital (Au4f) at 84.0 eV. The peak appears at 284.8 eV in surface-contaminated carbon. In contrast, when the carbon element charge density is high as in, for example, the carbon binding to a metallic element or a semi-metallic element, the C1s peak appears in a region below 284.5 eV. That is, when the C1s synthetic wave peak for SnCoC-containing material appears in a region below 284.5 eV, the carbon (C) contained in the SnCoC-containing material is at least partially binding to the other constituting elements, namely, the metallic element or the semi-metallic element.

Note that XPS uses, for example, a C1s peak for the calibration of the spectral energy axis. Generally, because the surface-contaminated carbon is present on the surface, the C1s peak of the surface-contaminated carbon is set to 284.8 eV, and used as the reference energy. In XPS, because the waveform of the C1s peak is obtained as the waveform that contains the peak of the surface-contaminated carbon and the peak of the carbon contained in the SnCoC-containing material, the peak of the surface-contaminated carbon and the peak of the carbon contained in the SnCoC-containing material are separated using, for example, commercially available software. In the waveform analysis, the position of the main peak on the lowest binding energy side is used as the reference energy (284.8 eV).

Other examples of the negative electrode material that can store and release lithium include metal oxides and polymer compounds that are capable of storing and releasing lithium. Examples of such metal oxides include iron oxide, ruthenium oxide, and molybdenum oxide. Examples of such polymer compounds include polyacetylene, polyaniline, and polypyrrole.

Further, the negative electrode material that can store and release lithium may be material, such as titanium, that forms a composite oxide with lithium.

Use of lithium metal as the negative electrode active material is also possible, and the lithium metal may be deposited and dissolved. The metal deposited and dissolved may be non-lithium metals such as magnesium and aluminum.

The negative electrode active material layer **34B** may be formed using, for example, any of a vapor-phase method, a liquid-phase method, a spray method, a calcining method, and coating, either individually or in combinations of two or more. The vapor-phase method may be, for example, a physical deposition method or a chemical deposition method, specifically, a vacuum deposition method, a sputter method, an ion plating method, a laser abrasion method, a chemical vapor deposition (CVD) method, or a plasma chemical vapor deposition method. Known techniques such as electroplating and non-electrolytic plating can be used as the liquid-phase method. The calcining method is a method in which, for example, a particulate negative electrode active material is mixed with other components such as a binder, dispersed in a solvent, and coated before it is subjected to a heat treatment at a temperature higher than the melting point of, for example, the binder. The calcining method also can be performed using known techniques, for example, such as an atmosphere calcining method, a reactive calcining method, and a hot-press calcining method.

When using lithium metal as the negative electrode active material, the negative electrode active material layer **34B** may be provided at the time of assembly, or may be formed after the assembly from the lithium metal that has deposited during the charging. Further, the negative electrode active material layer **34B** may be used as a collector, instead of the negative electrode collector **34A**.

(Separator)

The separator **35** is provided to isolate the positive electrode **33** and the negative electrode **34** from each other, and allows for passage of lithium ions while preventing current shorting caused by contacting of the electrodes. The separator **35** is configured using, for example, a porous film of synthetic resin such as polytetrafluoroethylene, polypropylene, and polyethylene, or a ceramic porous film. The separator **35** may be a laminate of two or more of these porous films.

(Electrolyte)

The electrolyte **36** is so-called a gel electrolyte that includes an electrolytic solution, and a polymer compound that swells by absorbing the electrolytic solution. In the gel electrolyte, the electrolytic solution is retained in the polymer compound. The gel electrolyte is preferable, because it provides high ion conductivity, and prevents leaking.

(Electrolytic Solution)

The electrolytic solution includes a solvent, and an electrolyte salt dissolved in the solvent. A polyacid and/or a polyacid compound are added to the electrolytic solution in advance. Thus, the electrolytic solution includes a polyacid and/or a polyacid compound dissolved in the solvent, prior to charging and discharging.

(Solvent)

The solvent may be, for example, a high-dielectric-constant solvent. Examples of high-dielectric-constant solvent include cyclic carbonate esters such as ethylene carbonate. Other examples of high-dielectric-constant solvent include lactones such as  $\gamma$ -butyrolactone and  $\gamma$ -valerolactone; lactams such as N-methylpyrrolidone; cyclic carbamic acid esters such as N-methylloxazolidinone; and sulfone compounds such as tetramethylenesulfone, which may be used in place of, or in addition to, cyclic carbonate esters.

A mixture of a high-dielectric-constant solvent and a low-viscosity solvent may be used as the solvent. Examples of low-viscosity solvent include chain carbonate esters such as ethylmethyl carbonate, diethyl carbonate, dimethyl carbonate, and methylpropyl carbonate; chain carboxylic acid esters such as methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, isomethyl butyrate, trimethylm-

ethyl acetate, and trimethylethyl acetate; chain amides such as N,N-dimethylacetamide; chain carbamic acid esters such as N,N-diethylcarbamic acid methyl, and N,N-diethylcarbamic acid ethyl; and ethers such as 1,2-dimethoxyethane, tetrahydrofuran, tetrahydropyran, and 1,3-dioxolan. The solvent is not limited to the compounds exemplified above, and a wide range of proposed compounds can be used.

(Electrolyte Salt)

The electrolyte salt includes, for example, one or more light metal salts such as lithium salts.

Examples of lithium salts include inorganic lithium salts such as lithium hexafluorophosphate ( $\text{LiPF}_6$ ), lithium tetrafluoroborate ( $\text{LiBF}_4$ ), lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ), lithium hexafluoroantimonate ( $\text{LiSbF}_6$ ), lithium perchloride ( $\text{LiClO}_4$ ), and lithium aluminum tetrachloride ( $\text{LiAlCl}_4$ ). Other examples of lithium salts include lithium salts of perfluoroalkane sulfonic acid derivatives, such as lithium trifluoromethanesulfonate ( $\text{CF}_3\text{SO}_3\text{Li}$ ), lithium bis(trifluoromethanesulfone)imide ( $((\text{CF}_3\text{SO}_2)_2\text{NLi})$ ), lithium bis(pentafluoromethanesulfone)imide ( $((\text{C}_2\text{F}_5\text{SO}_2)_2\text{NLi})$ ), lithium tris(trifluoromethanesulfone)methide ( $((\text{CF}_3\text{SO}_2)_3\text{CLi})$ ), and boron-containing lithium salts such as lithium tetrafluoroborate ( $\text{LiBF}_4$ ) and  $\text{LiB}(\text{C}_2\text{O}_4)_2$ .

(Polymer Compound)

Materials that gel by absorbing the solvent can be used as the polymer compounds. The polymer compounds may be used alone or as a mixture of two or more, or may be copolymers of two or more compounds. Examples of polymer compound include polyacrylonitrile, polyvinylidene fluoride, a copolymer of polyvinylidene fluoride and polyhexafluoropyrene, polytetrafluoroethylene, polyhexafluoropropylene, polyethylene oxide, polypropylene oxide, polyphosphazene, polysiloxane, polyvinyl acetate, polyvinyl alcohol, methyl polymethacrylate, polyacrylic acid, polymethacrylic acid, styrene-butadiene rubber, nitrile-butadiene rubber, polystyrene, and polycarbonate. These may be used alone or as mixtures of two or more. Polyacrylonitrile, polyvinylidene fluoride, polyhexafluoropropylene, and polyethylene oxide are particularly preferable for their electrochemical stability.

(Polyacid, Polyacid Compound)

(Heteropolyacid, Heteropolyacid Compound)

Heteropolyacid is a condensation product of two or more oxoacids. The preferred heteropolyacid and heteropolyacid compound are those of, for example, the Keggin structure, the Anderson structure, or the Dawson structure, in which the heteropolyacid ions easily dissolve in the battery solvent.

The heteropolyacid and/or heteropolyacid compound may be those including either a polyatom selected from element group (a), or a polyatom selected from element group (a), and in which some of the polyatoms are replaced with at least one selected from element group (b).

Element group (a): Mo, W, Nb, V

Element group (b): Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Tc, Rh, Cd, In, Sn, Ta, Re, Tl, Pb

Further, the heteropolyacid and/or heteropolyacid compound may be those including either a heteroatom selected from element group (c), or a heteroatom selected from element group (c), and in which some of the heteroatoms are replaced with at least one selected from element group (d).

Element group (c): B, Al, Si, P, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As

Element group (d): H, Be, B, C, Na, Al, Si, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Zr, Rh, Sn, Sb, Te, I, Re, Pt, Bi, Ce, Th, U, Np

Specific examples of heteropolyacid include heteropolytungstic acids such as phosphotungstic acid and silicotungstic acid, and heteropolymolybdic acids such as phosphomolyb-

dic acid and silicomolybdic acid. Examples of heteropolyacid compound include heteropolytungstic acid compounds such as sodium silicotungstate, sodium phosphotungstate, and ammonium phosphotungstate. Other examples of heteropolyacid compound include heteropolymolybdic acid compounds such as sodium phosphomolybdate, and ammonium phosphomolybdate. These heteropolyacids and heteropolyacid compounds may be used in combinations of two or more. Because these heteropolyacids and heteropolyacid compounds easily dissolve in the solvent and stably exist in the battery, they are unlikely to cause adverse effects, for example, by reacting with the other materials. Examples of heteropolyacid and/or heteropolyacid compound containing more than one polyelement include phosphovanadomolybdic acid, phosphotungstomolybdic acid, and silicotungstomolybdic acid. The heteropolyacid compound preferably includes cations, for example, such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{R}_4\text{N}^+$ , and  $\text{R}_4\text{P}^+$  (R is H or a hydrocarbon group of 10 or less carbon atoms). Preferably, the cation is  $\text{Li}^+$ , tetra-n-butylammonium, or tetra-n-butylphosphonium. Examples of such heteropolyacid compounds include heteropolytungstic acid compounds such as sodium silicotungstate, sodium phosphotungstate, ammonium phosphotungstate, and tetra-tetra-n-butyl phosphonium silicotungstate. Other examples of heteropolyacid compound include heteropolymolybdic acid compounds such as sodium phosphomolybdate, ammonium phosphomolybdate, and tri-tetra-n-butyl ammonium phosphomolybdate. Examples of the compound that includes more than one polyacid include materials such as tri-tetra-n-ammonium phosphotungstomolybdate. The heteropolyacids and heteropolyacid compounds may be used as mixtures of two or more. Because these heteropolyacids and heteropolyacid compounds easily dissolve in the solvent and stably exist in the battery, there are unlikely to cause adverse effects, for example, by reacting with the other materials.

Aside from the heteropolyacids and/or heteropolyacid compounds exemplified above, the polyacid and/or polyacid compound may be, for example, an isopolyacid and/or an isopolyacid compound that include one polyatom, or a polyacid and/or a polyacid compound that do not include a heteroatom but include one or more polyatoms, such as a polyacid and/or a polyacid compound that include two or more polyatoms but do not include a heteroatom.

For example, such polyacids and/or polyacid compounds may be those not including a heteroatom but including a polyatom selected from element group (a), or those including a polyatom selected from element group (a), and in which some of the polyatoms are replaced with at least one element selected from element group (b).

Element group (a): Mo, W, Nb, V

Element group (b): Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Tc, Rh, Cd, In, Sn, Ta, Re, Tl, Pb

Specific examples include tungstic acid(VI), and molybdic acid(VI), more specifically tungstic anhydride, molybdenum anhydride, and hydrates of these. Examples of hydrates include ortho-tungstic acids ( $\text{H}_2\text{WO}_4$ ), specifically tungstic acid monohydrate ( $\text{WO}_3 \cdot \text{H}_2\text{O}$ ); and ortho-molybdic acids ( $\text{H}_2\text{MoO}_4$ ), specifically molybdic acid dihydrates ( $\text{H}_4\text{MoO}_5$ ,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ ), and molybdic acid monohydrate ( $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ). It is also possible to use tungstic anhydride ( $\text{WO}_3$ ) having less, ultimately zero, hydrogen content than isopolyacids of the foregoing hydrates, such as metatungstic acid and paratungstic acid, or molybdenum anhydride ( $\text{MoO}_3$ ) having less, ultimately zero, hydrogen content than meta-molybdic acid, para-molybdic acid, and the like.

Use of heteropolyacids and/or heteropolyacid compounds as the polyacids and/or polyacid compounds is preferable,



because they have high solubility, for example, to the solvent used to adjust the positive electrode mixture and the negative electrode mixture, and to the nonaqueous solvent used for the electrolyte. The polyacids and/or polyacid compounds that do not contain heteroatoms tend to be slightly less effective than heteropolyacids and/or heteropolyacid compounds per added weight. However, because of low solubility to polar solvents, the polyacids and/or polyacid compounds that do not contain heteroatoms excel in coating characteristics such as coating viscoelasticity and aging when used for the positive electrode and the negative electrode, and are therefore useful from the industrial standpoint.

(Behaviors of Polyacid and/or Polyacid Compound in Response to Charging)

The following describes the behavior of the polyacid and/or polyacid compound in response to the charging of a nonaqueous electrolyte battery that includes the polyacid and/or polyacid compound added in advance to the electrolytic solution. In the following, descriptions will be made based on a nonaqueous electrolyte battery in which the polyacid and/or polyacid compound added in advance to the electrolytic solution are the heteropolyacid and/or heteropolyacid compound. In response to initial charging or preliminary charging, a coating that originates in the heteropolyacid and/or heteropolyacid compound is formed on the negative electrode **34**.

Specifically, in response to charging or preliminary charging, the heteropolyacid and/or heteropolyacid compound in the electrolytic solution undergo electrolysis, and as a result the compounds that originate in the heteropolyacid and/or heteropolyacid compound deposit on the surface of the negative electrode **34** and form an inorganic coating.

The heteropolyacid and/or heteropolyacid compound in the electrolytic solution undergo electrolysis in response to charging or preliminary charging according to the amounts of heteropolyacid and/or heteropolyacid compound added, and as a result compounds that originate in the heteropolyacid and/or heteropolyacid compound deposit on the surface of the positive electrode **33** and form an inorganic coating. The positive electrode active material layer **33B** includes a compound having a pyrrolidone skeleton, and thus has uniform conductivity. The uniform conductivity of the positive electrode active material layer **33B** promotes the inorganic coating that originates in the heteropolyacid and/or heteropolyacid compound to be evenly formed on the surface of the positive electrode **33**. With the evenly formed inorganic coating, deterioration of the electrode under a high-temperature environment can be suppressed.

Because the electrolytic solution of the heteropolyacid and/or heteropolyacid compound dissolved therein impregnates the negative electrode active material layer **34B**, the compounds that originate in the heteropolyacid and/or heteropolyacid compound may deposit in the negative electrode active material layer **34B** in response to charging or preliminary charging. The compounds that originate in the heteropolyacid and/or heteropolyacid compound may thus exist between negative electrode active material particles.

Similarly, because the electrolytic solution of the heteropolyacid and/or heteropolyacid compound dissolved therein impregnates the positive electrode active material layer **33B**, the compounds that originate in the heteropolyacid and/or heteropolyacid compound may deposit in the positive electrode active material layer **33B** in response to charging or preliminary charging. The compounds that originate in the heteropolyacid and/or heteropolyacid compound may thus exist between positive electrode active material particles.

The compounds that originate in the heteropolyacid and/or heteropolyacid compound include, for example, a polyacid and/or polyacid compound, or reduced products of a polyacid and/or polyacid compound, that are produced by the electrolysis of the heteropolyacid and/or heteropolyacid compound, and have poorer solubility than the heteropolyacid and/or heteropolyacid compound yet to undergo electrolysis.

Specifically, the polyacid and/or polyacid compound that deposit on the surface of the negative electrode **34** are amorphous. The amorphous heteropolyacid and/or heteropolyacid compound exist on the negative electrode surface as, for example, a gelled negative electrode coating formed by absorbing the nonaqueous electrolyte. The deposit including the polyacid and/or polyacid compound grows and deposits into, for example, a three-dimensional mesh structure on the negative electrode **34** at the time of preliminary charging or charging. The deposited polyacid and/or polyacid compound may be at least partially reduced.

The presence or absence of the inorganic coating that originates in the heteropolyacid and/or heteropolyacid compound can be confirmed by checking the positive electrode **33** removed by disassembling the nonaqueous electrolyte battery after charging or preliminary charging. For example, the deposition of the polyacid and/or polyacid compound confirmed upon checking the composition of the deposit formed on the positive electrode collector **33A** conveniently implies that the polyacid and/or polyacid compound have also deposited on the positive electrode active material layer **33B**, confirming the formation of an inorganic coating that originates in the heteropolyacid and/or heteropolyacid compound.

The presence or absence of the polyacid and/or polyacid compound can be confirmed by, for example, X-ray photoemission spectroscopy (XPS) analysis or time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this case, the battery is washed with dimethyl carbonate after disassembling the battery. The battery is washed to remove the low volatile solvent component and the electrolyte salt present on the surface. Preferably, sampling is performed in an inert atmosphere as much as possible.

(Amounts of Polyacid and/or Polyacid Compound Added)

Preferably, the polyacid and/or polyacid compound are added in amounts of from 0.02 mass % to 7.0 mass %, inclusive, with respect to the gel electrolyte **36**. Alternatively, the polyacid and/or polyacid compound are added preferably in amounts of from 0.014 mass % to 5.0 mass %, inclusive, with respect to the negative electrode active material layer **34B**. Note that the mass of the polyacid is the mass excluding the mass of the polyacid bonding water. Similarly, the mass of the polyacid compound is the mass excluding the mass of the polyacid compound bonding water.

Amounts of polyacid and/or polyacid compound below 0.02 mass % with respect to the gel electrolyte **36** fails to sufficiently form the coating that originates in the polyacid and/or polyacid compound. Polyacid and/or polyacid compound contents above 7.0 mass % with respect to the gel electrolyte **36** make the coating originating in the polyacid and/or polyacid compound too thick, and produce a coating resistance that inhibits charging and discharge. Further, amounts of polyacid and/or polyacid compound below 0.014 mass % with respect to the negative electrode active material layer **34B** fails to sufficiently form the coating that originates in the polyacid and/or polyacid compound. Polyacid and/or polyacid compound contents above 5.0 mass % with respect to the negative electrode active material layer **34B** make the coating originating in the polyacid and/or polyacid compound too thick, and produce a coating resistance that inhibits charging and discharge.

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(Content of the Compound Having a Pyrrolidone Skeleton)

Preferably, the content of the compound having a pyrrolidone skeleton is from 0.05 mass % to 1.0 mass %, inclusive, with respect to the positive electrode active material layer 33B. A content of the compound having a pyrrolidone skeleton below 0.05 mass % with respect to the positive electrode active material layer 33B fails to evenly form the coating that originates in the polyacid and/or polyacid compound. A content of the compound having a pyrrolidone skeleton above 1.0 mass % with respect to the positive electrode active material layer 33B increases the electrode resistance, and inhibits charging and discharge.

(Battery Producing Method)

The nonaqueous electrolyte battery is produced using, for example, three producing methods (first to third producing methods), as follows.

(First Producing Method)

(Production of Positive Electrode)

The fabrication begins with the positive electrode 33. For example, the positive electrode material, the binder, and the conductive agent are mixed to obtain a positive electrode mixture, which is then dispersed in an organic solvent, and formed into a paste positive electrode mixture slurry. The positive electrode mixture slurry is then evenly coated over the both surfaces of the positive electrode collector 33A using, for example, a doctor blade or a bar coater. After drying, the coating is compression molded using, for example, a roller press machine under optionally applied heat, and the positive electrode active material layer 33B is formed. The compression molding may be repeated multiple times.

(Production of Negative Electrode)

The negative electrode 34 is fabricated next. For example, the negative electrode material, the binder, and, optionally, the conductive agent are mixed to obtain a negative electrode mixture, which is then dispersed in an organic solvent, and formed into a paste negative electrode mixture slurry. The negative electrode mixture slurry is evenly coated over the both surfaces of the negative electrode collector 34A using, for example, a doctor blade or a bar coater. After drying, the coating is compression molded using, for example, a roller press machine under optionally applied heat, and the negative electrode active material layer 34B is formed.

A separately prepared precursor solution containing the electrolytic solution, the polymer compound, and the solvent is coated over the positive electrode 33 and the negative electrode 34, and the solvent is evaporated to form the gel electrolyte 36. The polyacid and/or polyacid compound are added during the preparation of the electrolytic solution. Then, the positive electrode lead 31 and the negative electrode lead 32 are attached to the positive electrode collector 33A and the negative electrode collector 34A, respectively.

The positive electrode 33 and the negative electrode 34 with the electrolyte 36 are then laminated via the separator 35, and wound along the longitudinal direction. The protective tape 37 is then bonded to the outermost periphery to fabricate the wound electrode unit 30. Finally, the wound electrode unit 30 is placed between, for example, a pair of film-like exterior members 40, and sealed therein by bonding the exterior members 40 at the peripheries by, for example, heatfusion. The adhesive film 41 is inserted between the positive and negative electrode leads 31 and 32 and the exterior members 40. This completes the nonaqueous electrolyte battery shown in FIGS. 1 and 2.

(Second Producing Method)

The positive electrode 33 and the negative electrode 34 are fabricated as in the first producing method. The positive elec-

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trode lead 31 and the negative electrode lead 32 are then attached to the positive electrode 33 and the negative electrode 34, respectively. The positive electrode 33 and the negative electrode 34 are then laminated and wound around with the separator 35 in between, and the protective tape 37 is bonded to the outermost periphery to obtain a wound unit as a precursor of the wound electrode unit 30.

The wound unit is then placed between a pair of film-like exterior members 40, which are then bonded by, for example, heatfusion at the peripheries, leaving one side open. As a result, the wound unit is housed inside the bag of the exterior member 40. Then, an electrolyte composition is prepared that includes the electrolytic solution, the raw material monomer of the polymer compound, a polymerization initiator, and optional materials such as a polymerization inhibitor, and the electrolyte composition is injected into the bag of the exterior member 40. The opening of the exterior member 40 is then sealed by, for example, heatfusion. The polyacid and/or polyacid compound are added during the preparation of the electrolytic solution. Finally, the monomer is heat polymerized into the polymer compound, and the gel electrolyte 36 is formed. This completes the nonaqueous electrolyte battery shown in FIGS. 1 and 2.

(Third Producing Method)

In the third producing method, a wound unit is formed and housed in the bag of the exterior member 40 in the same manner as in the second producing method, except that the polymer compound is coated on the both sides of the separator 35 in advance.

The polymer compound coated on the separator 35 may be, for example, a polymer that includes a vinylidene fluoride component, specifically, a homopolymer, a copolymer, or a multicomponent copolymer. Specific examples include polyvinylidene fluoride, binary copolymers that include vinylidene fluoride and hexafluoropropylene components, and ternary copolymers that include vinylidene fluoride, hexafluoropropylene, and chlorotrifluoroethylene components.

Note that the polymer compound may include one or more other polymer compounds, in addition to the polymer that includes a vinylidene fluoride component. Then, the electrolytic solution is prepared, and injected into the exterior member 40, and the opening of the exterior member 40 is sealed by, for example, heatfusion. The polyacid and/or polyacid compound are added during the preparation of the electrolytic solution. Finally, the exterior member 40 is heated under applied load to contact the separator 35 with the positive electrode 33 and the negative electrode 34 via the polymer compound. As a result, the electrolytic solution impregnates the polymer compound, causing the polymer compound to gel and form the electrolyte 36. This completes the nonaqueous electrolyte battery shown in FIGS. 1 and 2.

The nonaqueous electrolyte battery is, for example, a chargeable and dischargeable nonaqueous electrolyte secondary battery. For example, upon charging, the positive electrode 33 releases lithium ions, and the lithium ions are stored in the negative electrode 34 via the electrolyte 36. Upon discharge, the negative electrode 34 releases lithium ions, and the lithium ions are stored in the positive electrode 33 via the electrolyte 36. Alternatively, for example, the lithium ions in the electrolyte 36 accept electrons upon charging, and deposit as lithium metal on the negative electrode 34. Upon discharge, the lithium metal on the negative electrode 34 releases electrons, which then dissolve in the electrolyte 36 in the form of lithium ions. Further, for example, the positive electrode 33 releases lithium ions upon charging, and the lithium ions are stored in the negative electrode 34 via the electrolyte 36 as the

lithium metal deposits in the process of charging. Upon discharge, the lithium metal deposited on the negative electrode **34** releases electrons, which then dissolve in the electrolyte **36** in the form of lithium ions, and the lithium ions stored in the negative electrode **34** are released in the process of discharge, and stored in the positive electrode **33** via the electrolyte **36**.

(Variations)

In the exemplary configuration of the nonaqueous electrolyte battery described above, the polyacid and/or polyacid compound were added to the electrolytic solution in advance. However, the polyacid and/or polyacid compound may be added in advance to the constituting elements of the battery other than the electrolytic solution.

The first to third variations below describe exemplary configurations of the nonaqueous electrolyte battery in which the polyacid and/or polyacid compound are added in advance to the constituting elements of the battery other than the electrolytic solution. Note that the following descriptions primarily deal with differences from the foregoing exemplary configuration of the nonaqueous electrolyte battery (the polyacid and/or polyacid compound being added in advance to the electrolytic solution), and descriptions concerning the foregoing exemplary configuration of the nonaqueous electrolyte battery will be omitted as appropriate.

(First Variation: Polyacid and/or Polyacid Compound Added to Positive Electrode Active Material Layer)

The first variation does not differ from the foregoing exemplary configuration of the nonaqueous electrolyte battery, except that the polyacid and/or polyacid compound are added in advance not to the electrolytic solution but to the positive electrode active material layer.

(Method of Production of Positive Electrode **33**)

In the first variation, the positive electrode **33** is fabricated in the following manner. First, the positive electrode material, the binder, and the conductive agent are mixed, and the polyacid and/or polyacid compound are dissolved in an organic solvent such as N-methyl-2-pyrrolidone to prepare a solution. The solution is mixed with the mixture of the positive electrode material, the binder, and the conductive agent to prepare a positive electrode mixture, which is then dispersed in an organic solvent such as N-methyl-2-pyrrolidone to obtain a positive electrode mixture slurry. The positive electrode mixture slurry is evenly coated over the both surfaces of the positive electrode collector **33A** using, for example, a doctor blade or a bar coater. After drying, the coating is compression molded using, for example, a roller press machine under optionally applied heat, and the positive electrode active material layer **33B** is formed.

(Positive Electrode Active Material Layer **33B**)

In the first variation, prior to charging and discharge, the positive electrode active material layer **33B** includes the polyacid and/or polyacid compound, and one or more positive electrode materials (positive electrode active materials) capable of storing and releasing lithium. As required, the positive electrode active material layer **33B** may also include other materials such as a binder and a conductive agent.

(Behaviors of Polyacid and/or Polyacid Compound in Response to Charging)

The electrolytic solution impregnates the positive electrode active material layer **33B**, and thus the polyacid and/or polyacid compound contained in the positive electrode active material layer **33B** dissolve into the electrolytic solution. In response to initial charging or preliminary charging, a coating that originates in the polyacid and/or polyacid compound dissolved into the electrolytic solution is formed on the negative electrode **34**.

Specifically, as a result of initial charging or preliminary charging, the polyacid and/or polyacid compound dissolved in the electrolytic solution undergo electrolysis, and compounds that originate in the polyacid and/or polyacid compound deposit on the surface of the negative electrode **34** and form an inorganic coating.

Further, as a result of initial charging or preliminary charging, the polyacid and/or polyacid compound dissolved in the electrolytic solution undergo electrolysis, and compounds that originate in the polyacid and/or polyacid compound deposit on the surface of the positive electrode **33** and form an inorganic coating. The positive electrode active material layer **33B** includes a compound having a pyrrolidone skeleton, and thus has uniform conductivity. The uniform conductivity of the positive electrode active material layer **33B** promotes the inorganic coating that originates in the polyacid and/or polyacid compound to be evenly formed on the surface of the positive electrode **33**. With the evenly formed inorganic coating, deterioration of the electrode under a high-temperature environment can be suppressed.

Because the polyacid and/or polyacid compound dissolve into the electrolytic solution that impregnates the negative electrode active material layer **34B**, compounds that originate in the polyacid and/or polyacid compound may deposit in the negative electrode active material layer **34B** in response to charging or preliminary charging. The compounds that originate in the polyacid and/or polyacid compound may thus exist between negative electrode active material particles.

Further, because the polyacid and/or polyacid compound dissolve into the electrolytic solution that impregnates the positive electrode active material layer **33B**, compounds that originate in the polyacid and/or polyacid compound may deposit in the positive electrode active material layer **33B** in response to charging or preliminary charging. The compounds that originate in the polyacid and/or polyacid compound may thus exist between the positive electrode active material particles.

(Second Variation: Polyacid and/or Polyacid Compound Added to Negative Electrode Active Material Layer)

The second variation does not differ from the foregoing exemplary configuration of the nonaqueous electrolyte battery, except that the polyacid and/or polyacid compound are added in advance not to the electrolytic solution but to the negative electrode active material layer **34B**.

(Method of Production of Negative Electrode **34**)

In the second variation, the negative electrode **34** is fabricated in the following manner. First, the negative electrode material, the binder, and, optionally, the conductive agent are mixed. Separately, the polyacid and/or polyacid compound are dissolved to prepare a solution. The solution is mixed with the mixture to obtain a negative electrode mixture, which is then dispersed in an organic solvent such as N-methyl-2-pyrrolidone to obtain a paste negative electrode mixture slurry. The negative electrode mixture slurry is evenly coated over the both surfaces of the negative electrode collector **34A** using, for example, a doctor blade or a bar coater. After drying, the coating is compression molded using, for example, a roller press machine under optionally applied heat, and the negative electrode active material layer **34B** is formed.

(Negative Electrode Active Material Layer **34B**)

In the second variation, prior to charging and discharge, the negative electrode active material layer **34B** includes the polyacid and/or polyacid compound, and one or more negative electrode materials (negative electrode active materials)

capable of storing and releasing lithium. Other materials such as a binder and a conductive agent also may be contained, as required.

(Behaviors of Polyacid and/or Polyacid Compound in Response to Charging)

The electrolytic solution impregnates the negative electrode active material layer **34B**, and thus the polyacid and/or polyacid compound contained in the negative electrode active material layer **34B** dissolve into the electrolytic solution. As a result of initial charging or preliminary charging, an inorganic coating that originates in the polyacid and/or polyacid compound dissolved into the electrolytic solution is formed on the negative electrode **34**.

Specifically, as a result of initial charging or preliminary charging, the polyacid and/or polyacid compound dissolved in the electrolytic solution undergo electrolysis, and compounds that originate in the polyacid and/or polyacid compound deposit on the surface of the negative electrode **34** and form an inorganic coating.

Further, the polyacid and/or polyacid compound dissolved in the electrolytic solution undergo electrolysis in response to initial charging or preliminary charging, according to the amounts of polyacid and/or polyacid compound added. As a result, compounds that originate in the polyacid and/or polyacid compound deposit on the surface of the positive electrode **33**, and form an inorganic coating. The positive electrode active material layer **33B** includes a compound having a pyrrolidone skeleton, and thus has uniform conductivity. The uniform conductivity of the positive electrode active material layer **33B** promotes the inorganic coating that originates in the polyacid and/or polyacid compound to be evenly formed on the surface of the positive electrode **33**. With the evenly formed inorganic coating, deterioration of the electrode under a high-temperature environment can be suppressed.

Because the polyacid and/or polyacid compound dissolve into the electrolytic solution that impregnates the negative electrode active material layer **34B**, compounds that originate in the polyacid and/or polyacid compound may deposit in the negative electrode active material layer **34B** in response to charging or preliminary charging. The compounds that originate in the polyacid and/or polyacid compound may thus exist between negative electrode active material particles.

Further, because the polyacid and/or polyacid compound dissolve into the electrolytic solution that impregnates the positive electrode active material layer **33B**, compounds that originate in the polyacid and/or polyacid compound may deposit in the positive electrode active material layer **33B** in response to charging or preliminary charging. The compounds that originate in the polyacid and/or polyacid compound may thus exist between positive electrode active material particles.

(Third Variation)

The third variation does not differ from the foregoing exemplary configuration of the nonaqueous electrolyte battery, except that the polyacid and/or polyacid compound are added in advance not to the electrolytic solution but to the separator **35**.

In the third variation, the polyacid and/or polyacid compound are added in advance to the separator **35**. For example, the polyacid and/or polyacid compound are added in advance to the separator **35** in the following manner.

The separator **35** is dipped in a solution of the polyacid and/or polyacid compound dissolved in a polar organic solvent such as dimethyl carbonate. After being impregnated with the solution, the separator **35** is dried in a vacuum atmo-

sphere. As a result, the polyacid and/or polyacid compound deposit on the surface or in the pores of the separator **35**.

(Behaviors of Polyacid and/or Polyacid Compound in Response to Charging)

The separator **35** is impregnated with the electrolytic solution, and thus the polyacid and/or polyacid compound added to the separator **35** dissolve into the electrolytic solution. As a result of initial charging or preliminary charging, an inorganic coating that originates in the polyacid and/or polyacid compound dissolved in the electrolytic solution is formed on the negative electrode **34**.

Specifically, as a result of initial charging or preliminary charging, the polyacid and/or polyacid compound dissolved in the electrolytic solution undergo electrolysis, and compounds that originate in the polyacid and/or polyacid compound deposit on the surface of the negative electrode **34** and form an inorganic coating.

Further, the polyacid and/or polyacid compound dissolved in the electrolytic solution undergo electrolysis in response to initial charging or preliminary charging, according to the amounts of polyacid and/or polyacid compound added. As a result, compounds that originate in the polyacid and/or polyacid compound deposit on the surface of the positive electrode **33** and form an inorganic coating. The positive electrode active material layer **33B** includes a compound having a pyrrolidone skeleton, and thus has uniform conductivity. The uniform conductivity of the positive electrode active material layer **33B** promotes the inorganic coating that originates in the polyacid and/or polyacid compound to be evenly formed on the surface of the positive electrode **33**. With the evenly formed inorganic coating, deterioration of the electrode under a high-temperature environment can be suppressed.

Because the polyacid and/or polyacid compound dissolve into the electrolytic solution that impregnates the negative electrode active material layer **34B**, compounds that originate in the polyacid and/or polyacid compound may deposit in the negative electrode active material layer **34B** in response to charging or preliminary charging. The compounds that originate in the polyacid and/or polyacid compound may thus exist between negative electrode active material particles.

Further, because the polyacid and/or polyacid compound dissolve into the electrolytic solution that impregnates the positive electrode active material layer **33B**, compounds that originate in the polyacid and/or polyacid compound may deposit in the positive electrode active material layer **33B** in response to charging or preliminary charging. The compounds that originate in the polyacid and/or polyacid compound may thus exist between positive electrode active material particles.

(Effects)

With the nonaqueous electrolyte battery according to First Embodiment, capacity decrease during high-temperature storage can be suppressed.

## 2. Second Embodiment

A nonaqueous electrolyte battery according to Second Embodiment is described below. The nonaqueous electrolyte battery according to Second Embodiment does not differ from the nonaqueous electrolyte battery of First Embodiment, except that the electrolytic solution is directly used instead of being retained in the polymer compound (electrolyte **36**). Accordingly, the following detailed descriptions mainly deal with the difference from First Embodiment.

(Configuration of Nonaqueous Electrolyte Battery)

The nonaqueous electrolyte battery according to Second Embodiment uses the electrolytic solution instead of the gel electrolyte **36**. Thus, the wound electrode unit **30** does not

include the electrolyte 36, and instead includes the electrolytic solution impregnating the separator 35.

(Method of Production of Nonaqueous Electrolyte Battery)

The nonaqueous electrolyte battery can be produced, for example, as follows.

First, for example, the positive electrode active material, the binder, and the conductive agent are mixed to prepare a positive electrode mixture, which is then dispersed in a solvent such as N-methyl-2-pyrrolidone to obtain a positive electrode mixture slurry. The positive electrode mixture slurry coated on the both sides, dried, and compression molded to form the positive electrode active material layer 33B and obtain the positive electrode 33. Thereafter, for example, the positive electrode lead 31 is attached to the positive electrode collector 33A, for example, by ultrasonic welding or spot welding.

For example, the negative electrode material and the binder are mixed to prepare a negative electrode mixture, which is then dispersed in a solvent such as N-methyl-2-pyrrolidone to obtain a negative electrode mixture slurry. The negative electrode mixture slurry is coated on the both sides of the negative electrode collector 34A, dried, and compression molded to form the negative electrode active material layer 34B and obtain the negative electrode 34. Thereafter, for example, the negative electrode lead 32 is attached to the negative electrode collector 34A, for example, by ultrasonic welding or spot welding.

The positive electrode 33 and the negative electrode 34 are wound around with the separator 35 in between, and installed in the exterior member 40. The electrolytic solution is then injected into the exterior member 40, and the exterior member 40 is sealed. As a result, the nonaqueous electrolyte battery shown in FIGS. 1 and 2 is obtained.

(Effects)

The effects obtained in First Embodiment also can be obtained in Second Embodiment.

### 3. Third Embodiment

(Configuration of Nonaqueous Electrolyte Battery)

A configuration of a nonaqueous electrolyte battery according to Third Embodiment is described below with reference to FIGS. 3 to 4. FIG. 3 represents an exemplary configuration of the nonaqueous electrolyte battery according to Third Embodiment. The nonaqueous electrolyte battery is of a cylindrical type, in which a wound electrode unit 20 obtained by winding a belt-like positive electrode 21 and a belt-like negative electrode 22 via a separator 23 is placed in a substantially hollow cylindrical battery canister (cylindrical canister) 11 provided as an exterior member. The separator 23 is impregnated with the liquid electrolyte electrolytic solution. The battery canister 11 is made of, for example, nickel (Ni)-plated iron (Fe), and has a closed end and an open end. Inside the battery canister 11, a pair of insulating plates 12 and 13 is disposed on the both sides of the wound electrode unit 20, perpendicularly to the rolled surface.

The battery canister 11 is sealed with a battery lid 14 fastened to the open end of the battery canister 11 by swaging via a gasket 17, together with a safety valve mechanism 15 and a heat-sensitive resistive (PTC: Positive Temperature Coefficient) element 16 provided inside the battery lid 14. The battery lid 14 is formed using, for example, the same or similar materials used for the battery canister 11. The safety valve mechanism 15 is electrically connected to the battery lid 14 via the heat-sensitive resistive element 16, and cuts off the electrical connection between the battery lid 14 and the wound electrode unit 20 by the inversion of a disk plate 15A, when the pressure inside the battery reaches a certain level as

a result of internal shorting or external heat. The heat-sensitive resistive element 16 increases its resistance value under elevated temperatures, and restricts current to prevent abnormal heating due to overcurrent. The gasket 17 is formed using, for example, insulating material, and is asphalt-coated.

The wound electrode unit 20 is wound around, for example, a center pin 24. The positive electrode 21 of the wound electrode unit 20 is connected to a positive electrode lead 25 of, for example, aluminum (Al), and the negative electrode 22 is connected to a negative electrode lead 26 of, for example, nickel (Ni). The positive electrode lead 25 is electrically connected to the battery lid 14 by being welded to the safety valve mechanism 15. The negative electrode lead 26 is electrically connected to the battery canister 11 by being welded thereto.

FIG. 4 is an enlarged cross sectional view illustrating a portion of the wound electrode unit 20 shown in FIG. 3. The wound electrode unit 20 is the wound laminate of the positive electrode 21 and the negative electrode 22 via the separator 23.

The positive electrode 21 includes, for example, a positive electrode collector 21A, and a positive electrode active material layer 21B formed on the both surfaces of the positive electrode collector 21A. The negative electrode 22 includes, for example, a negative electrode collector 22A, and a negative electrode active material layer 22B formed on the both surfaces of the negative electrode collector 22A. The positive electrode collector 21A, the positive electrode active material layer 21B, the negative electrode collector 22A, the negative electrode active material layer 22B, the separator 23, and the electrolytic solution have the same configurations as the positive electrode collector 33A, the positive electrode active material layer 33B, the negative electrode collector 34A, the negative electrode active material layer 34B, the separator 35, and the electrolytic solution, respectively, of First Embodiment.

(Method of Production of Nonaqueous Electrolyte Battery)

The nonaqueous electrolyte battery can be produced as follows.

The positive electrode 21 is fabricated in the same manner as the positive electrode 33 of First Embodiment. The negative electrode 22 is fabricated in the same manner as the negative electrode 34 of First Embodiment.

The positive electrode lead 25 and the negative electrode lead 26 are attached to the positive electrode collector 21A and to the negative electrode collector 22A, respectively, by, for example, welding. The positive electrode 21 and the negative electrode 22 are then wound around via the separator 23, and the positive electrode lead 25 and the negative electrode lead 26 are welded at the front end to the safety valve mechanism 15 and to the battery canister 11, respectively. The roll of the positive electrode 21 and the negative electrode 22 is then sandwiched between the insulating plates 12 and 13, and housed inside the battery canister 11. With the positive electrode 21 and the negative electrode 22 housed inside the battery canister 11, the electrolyte is injected into the battery canister 11, and the separator 23 is impregnated with the electrolytic solution. The battery lid 14, the safety valve mechanism 15, and the heat-sensitive resistive element 16 are then fastened to the open end of the battery canister 11 by swaging via the gasket 17. As a result, the nonaqueous electrolyte battery shown in FIG. 3 is obtained.

(Effects)

The effects obtained in First Embodiment also can be obtained in Third Embodiment.

#### 4. Fourth Embodiment

(Configuration of Nonaqueous Electrolyte Battery)

FIG. 5 is an exploded perspective view representing an exemplary configuration of a nonaqueous electrolyte battery according to Fourth Embodiment. As illustrated in FIG. 5, the nonaqueous electrolyte battery includes a battery element 71 to which a positive electrode lead 73 and a negative electrode lead 74 are attached, and the battery element 71 is housed inside a film-like exterior member 72, in order to make the battery small, lightweight, and thin.

The positive electrode lead 73 and the negative electrode lead 74 are provided to extend out of the exterior member 72, for example, in the same direction.

FIG. 6 is a perspective view illustrating an example of an appearance of the battery element 71. FIG. 7 is a cross sectional view illustrating an exemplary configuration of the battery element 71. As illustrated in FIGS. 6 and 7, the battery element 71 is an electrode laminate that includes a positive electrode 81 and a negative electrode 82 laminated via a separator 83, and the battery element 71 is impregnated with an electrolytic solution.

The positive electrode 81 is structured to include, for example, a positive electrode active material layer 81B provided on the both sides of a double-sided positive electrode collector 81A. As illustrated in FIG. 8, the positive electrode 81 includes a rectangular electrode portion, and a collector exposed portion 81C that extends from one side of the electrode portion. The collector exposed portion 81C does not include the positive electrode active material layer 81B, and the positive electrode collector 81A is exposed. The collector exposed portion 81C is electrically connected to the positive electrode lead 73. Though not illustrated, a region with the positive electrode active material layer 81B may be provided only on one side of the positive electrode collector 81A.

The negative electrode 82 is structured to include, for example, a negative electrode active material layer 82B provided on the both sides of a double-sided negative electrode collector 82A. As illustrated in FIG. 9, the negative electrode 82 includes a rectangular electrode portion, and a collector exposed portion 82C that extends from one side of the electrode portion. The collector exposed portion 82C does not include the negative electrode active material layer 82B, and the negative electrode collector 82A is exposed. The collector exposed portion 82C is electrically connected to the negative electrode lead 74. Though not illustrated, a region with the negative electrode active material layer 82B may be provided only on one side of the negative electrode collector 82A.

As illustrated in FIG. 10, the separator 83 is rectangular in shape, for example.

The positive electrode collector 81A, the positive electrode active material layer 81B, the negative electrode collector 82A, the negative electrode active material layer 82B, the separator 83, and the electrolytic solution are made of the same materials as those used for the positive electrode collector 21A, the positive electrode active material layer 21B, the negative electrode collector 22A, the negative electrode active material layer 22B, the separator 23, and the electrolytic solution, respectively, of First Embodiment.

(Method of Production of Nonaqueous Electrolyte Battery)

The nonaqueous electrolyte battery of the foregoing configuration can be produced as follows.

(Fabrication of Positive Electrode)

The positive electrode 81 is fabricated in the following manner. First, for example, the positive electrode material, the binder, and the conductive agent are mixed to prepare a positive electrode mixture, which is then dispersed in an organic solvent such as N-methylpyrrolidone to obtain a paste positive electrode mixture slurry. The positive electrode mixture slurry is then coated over the both surfaces of the positive electrode collector 81A, dried, and pressed into the positive electrode active material layer 81B. The positive electrode active material layer 81B is cut into the shape shown in, for example, FIG. 8, and the positive electrode 81 is obtained.

(Fabrication of Negative Electrode)

The negative electrode 82 is fabricated in the following manner. First, for example, the negative electrode material, the binder, and the conductive agent are mixed to prepare a negative electrode mixture, which is then dispersed in an organic solvent such as N-methylpyrrolidone to obtain a paste negative electrode mixture slurry. The negative electrode mixture slurry is then coated over the both surfaces of the negative electrode collector 82A, dried, and pressed into the negative electrode active material layer 82B. The negative electrode active material layer 82B is then cut into the shape shown in, for example, FIG. 9, and the negative electrode 82 is obtained.

(Fabrication of Battery Element)

The battery element 71 is fabricated in the following manner. First, for example, a polypropylene microporous film is cut into the shape shown in FIG. 10 to fabricate the separator 83. The sheets of the negative electrode 82, the positive electrode 81, and the separator 83 obtained as above are then laminated as illustrated in, for example, FIG. 11, in repeating units of the negative electrode 82, the separator 83, and the positive electrode 81. As a result, the battery element 71 is obtained.

Then, the collector exposed portion 82C of the positive electrode 81 is welded to the positive electrode lead 73. Similarly, the collector exposed portion 82C of the negative electrode 82 is welded to the negative electrode lead 74. The electrolytic solution is then impregnated in the battery element 71, and the battery element 71 is installed in the exterior member 72, which is then sealed at the peripheries by, for example, heat fusion. Here, the positive electrode lead 73 and the negative electrode lead 74 stick out of the exterior member 72 through the heatfused portion, and serve as the positive and negative electrode terminals, respectively. As a result, the nonaqueous electrolyte battery is obtained.

(Effects)

The effects obtained in First Embodiment also can be obtained in Fourth Embodiment.

#### 5. Fifth Embodiment

Fifth Embodiment is described below. The nonaqueous electrolyte battery according to Fifth Embodiment has the same configuration as the nonaqueous electrolyte battery of Fourth Embodiment, except that a gel electrolyte layer is used instead of the electrolytic solution. Note that elements already described in Fourth Embodiment are given the same reference numerals, and explanations thereof are omitted.

(Structure of Nonaqueous Electrolyte Battery)

FIG. 11 is a cross sectional view illustrating an exemplary configuration of the battery element used for the nonaqueous electrolyte secondary battery of Fifth Embodiment. A battery element 85 includes the positive electrode 81 and the negative electrode 82 laminated via the separator 83 and an electrolyte layer 84.

The electrolyte layer 84 is a gel layer that includes an electrolytic solution, and a polymer compound provided as a

body that retains the electrolytic solution. The gel electrolyte layer **84** is preferred because it can provide high ion conductivity and prevent battery leakage. The polymer compound has the same configuration as described in conjunction with the nonaqueous electrolyte battery of First Embodiment.

(Method of Production of Nonaqueous Electrolyte Battery)

The nonaqueous electrolyte battery of the foregoing configuration can be produced, for example, as follows.

First, the positive electrode **81** and the negative electrode **82** are each coated with a precursor solution that includes a solvent, an electrolyte salt, a polymer compound, and a mixed solvent. The mixed solvent is then evaporated to form the electrolyte layer **84**. The nonaqueous electrolyte battery can then be obtained by following the steps described in Fourth Embodiment, except for using the positive electrode **81** and the negative electrode **82** provided with the electrolyte layer **84**.

(Effects)

The effects obtained in Fourth Embodiment also can be obtained in Fifth Embodiment.

### EXAMPLES

The following specifically describes the application based on Examples. Note, however, that the application is not limited by the following Examples. In the following, the mass of the heteropolyacid is the mass excluding the mass of the heteropolyacid bonding water. The mass of the heteropolyacid compound is the mass excluding the mass of the heteropolyacid compound bonding water.

<Sample 1-1>

First, a paste mixture layer containing active material was coated and formed on a metal foil provided as a belt-like collector. After drying, the coated foil was fabricated into a belt-like electrode by compression molding using a pressure device. Specifically, an aluminum foil having a thickness of 12  $\mu\text{m}$  was used as the positive electrode collector, and a positive electrode active material was prepared by mixing 94 parts by mass of lithium nickel oxide, 3 parts by mass of the conductive agent graphite, 3 parts by mass of the binder polyvinylidene fluoride (PVDF), and polyvinylpyrrolidone (PVP). The dispersion solvent N-methyl-2-pyrrolidone was then added to the mixture, and a paste positive electrode mixture was obtained. The amount of polyvinylpyrrolidone (PVP) in the mixture was adjusted to 0.01 mass % with respect to the positive electrode mixture.

The positive electrode mixture paste was then coated over the both surfaces of the belt-like aluminum foil. After drying, the coated foil was molded into a predetermined thickness using a pressure roll machine to obtain the positive electrode.

The negative electrode active material was prepared by mixing 90 mass % of artificial graphite, and 10 mass % of the binder PVdF. The dispersion solvent N-methyl-2-pyrrolidone was then added to the mixture, and a paste negative electrode mixture was obtained. The negative electrode mixture paste was then coated over the both surfaces of a belt-like 10  $\mu\text{m}$ -thick copper foil. The coated foil was molded into a predetermined thickness using a pressure roll machine to obtain the negative electrode.

A solution prepared by mixing and dissolving polyvinylidene fluoride (PVdF) in an electrolytic solution was coated on the surface of the positive electrode or the negative electrode, and the electrode was dried in dry air. The electrolytic solution was prepared by dissolving  $\text{LiPF}_6$  in 1 mol/l in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC), and then dissolving as the heteropolyacid and/or heteropolyacid compound silicotungstic acid ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ). The amount of silicotungstic acid ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ) in the mixture was adjusted to 0.01 mass % with respect to the gel electrolyte.

The belt-like positive and negative electrodes so fabricated were laminated via a microporous separator, wound multiple times in an oval shape, and housed in an aluminum laminate housing to obtain a thin battery measuring 34 mm in width, 50 mm in length, and 3.8 mm in thickness.

<Samples 1-2 to 1-20>

Thin batteries of samples 1-1 to 1-20 were fabricated as in sample 1-1, except that the silicotungstic acid ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ) and polyvinylpyrrolidone (PVP) contents were changed as shown in Table 1. In Table 1, the amount in mass % of the silicotungstic acid ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ) with respect to the negative electrode mixture is also presented.

(Capacity Measurement after High-Temperature Storage)

Each thin battery was charged by constant-current/constant-voltage charging at 400 mA/4.2 V, and discharge capacity was measured after the constant current discharge at 200 mA/2.5 V. Thereafter, the battery was charged by constant-current/constant-voltage charging at 400 mA/4.2 V, and placed and stored in a 90° C. oven for 7 days. After the storage, the cell was taken out, and the cell capacity was measured again. The percentage decrease of the discharge capacity of the stored cell with respect to the original cell discharge capacity was then determined. The measurement results are presented in Table 1.

TABLE 1

		PVP content (mass %)					
		0	0.01	0.05	0.1	1.0	2.0
SiW content (mass %)	0 (0)	Sample 1-21	Sample 1-26	Sample 1-27	Sample 1-28	Sample 1-29	Sample 1-30
	0.01 (0.007)	Sample 1-22	Sample 1-1	Sample 1-5	Sample 1-9	Sample 1-13	Sample 1-17
	0.02 (0.014)	Sample 1-23	Sample 1-2	Sample 1-6	Sample 1-10	Sample 1-14	Sample 1-18
	7 (5)	Sample 1-24	Sample 1-3	Sample 1-7	Sample 1-11	Sample 1-15	Sample 1-19
	14 (10)	Sample 1-25	Sample 1-4	Sample 1-8	Sample 1-12	Sample 1-16	Sample 1-20
Percentage capacity decrease after 90° C. storage for 7 days							
SiW content (mass %)	0 (0)	12%	11%	12%	11%	12%	10%
	0.01 (0.007)	9%	10%	9%	11%	10%	12%
	0.02 (0.014)	10%	11%	5%	5%	6%	10%
	7 (5)	9%	11%	6%	6%	7%	10%
	14 (10)	14%	13%	12%	12%	13%	16%

The numbers in parentheses are mass % with respect to negative electrode mixture  
SiW:  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$

As shown in Table 1, it was found that capacity decrease during high-temperature storage could be suppressed by addition of silicotungstic acid ( $H_4SiW_{12}O_{40}$ ) in the battery and by inclusion of PVP in the positive electrode active material layer. The effect of suppressing capacity decrease during high-temperature storage was particularly prominent in samples 1-6 to 1-7, samples 1-10 to 1-11, and samples 1-14 to 1-15.

(Variation of Electrode Surface Resistance)

#### Test Example 1-1

A 12  $\mu$ m-thick aluminum foil was used as the positive electrode collector, and a positive electrode active material was prepared by mixing 94 parts by mass of lithium nickel oxide, 3 parts by mass of the conductive agent graphite, 2.5 parts by mass of the binder polyvinylidene fluoride (PVDF), and 0.5 parts by mass of polyvinylpyrrolidone (PVP). The dispersion solvent N-methyl-2-pyrrolidone was then added to the mixture to obtain a paste positive electrode mixture. The positive electrode mixture paste was then coated over the both surfaces of the belt-like aluminum foil. The coated foil was dried, and molded into a predetermined thickness using a pressure roll machine to obtain the positive electrode. The surface resistance of the positive electrode was measured, and variation of surface resistance was evaluated.

#### Test Example 1-2

The positive electrode was fabricated as in Test Example 1-1 except that polyvinylidene fluoride was mixed in an increased amount to compensate for the absence of polyvinylpyrrolidone (PVP) in the mixture. The surface resistance of the positive electrode was then measured as in Test Example 1-1, and variation of surface resistance was evaluated.

The measurement results are presented in FIG. 12. As shown in FIG. 12, surface resistance variation was smaller in the positive electrode that contained polyvinylpyrrolidone (PVP) in the positive electrode mixture than in the positive electrode that did not contain polyvinylpyrrolidone (PVP) in the positive electrode mixture. It was therefore found that the positive electrode that contained polyvinylpyrrolidone (PVP) in the positive electrode mixture, with its small surface resistance variation, was effective at promoting formation of an even coating that originates in the heteropolyacid and/or heteropolyacid compound. The coating formed on the positive electrode remains stable during high-temperature storage, and can thus suppress capacity decrease during high-temperature storage.

#### 6. Other Embodiments

While the application has been described with respect to certain embodiments and examples, the application is not limited by these embodiments and examples, and various modifications and applications are possible within the scope of the application.

For example, while the foregoing Embodiments and Examples described batteries of a laminate film type, batteries of a cylindrical battery structure, batteries of a wound electrode structure, and batteries of a stacked electrode structure, the application is not limited by these. For example, the application is also applicable to and equally effective in other battery structures, including batteries of rectangular, coin, and button structures.

It should be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such

changes and modifications can be made without departing from the spirit and scope and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

The invention claimed is:

1. A nonaqueous electrolyte battery comprising:

a positive electrode having a positive electrode active material layer that includes a positive electrode active material, a binder, and a compound having a pyrrolidone skeleton;

a negative electrode having a negative electrode active material layer;

a nonaqueous electrolyte that includes a solvent and an electrolyte salt; and

at least one of a heteropolyacid and a heteropolyacid compound contained inside the battery.

2. The nonaqueous electrolyte battery according to claim 1, wherein the compound having a pyrrolidone skeleton is polyvinylpyrrolidone (PVP).

3. The nonaqueous electrolyte battery according to claim 1, wherein the compound having a pyrrolidone skeleton is contained in a content of from 0.05 mass % to 1.0 mass %, inclusive, with respect to a mass of the positive electrode active material layer, and

wherein the at least one of a heteropolyacid and a heteropolyacid compound is added in an amount of from 0.014 mass % to 5.0 mass %, inclusive, with respect to a mass of the negative electrode active material layer.

4. The nonaqueous electrolyte battery according to claim 1, wherein the nonaqueous electrolyte is a gel electrolyte that comprises:

an electrolytic solution that includes the solvent and the electrolyte salt; and

a polymer compound that swells by absorbing the electrolytic solution.

5. The nonaqueous electrolyte battery according to claim 4, wherein the at least one of a heteropolyacid and a heteropolyacid compound is added to the gel electrolyte, wherein the compound having a pyrrolidone skeleton is added in an amount of from 0.05 mass % to 1.0 mass %, inclusive, with respect to a mass of the positive electrode active material layer, and

wherein the at least one of a heteropolyacid and a heteropolyacid compound is contained in a content of from 0.02 mass % to 7.0 mass %, inclusive, with respect to a mass of the gel electrolyte.

6. The nonaqueous electrolyte battery according to claim 1, wherein the heteropolyacid and the heteropolyacid compound each include a heteroatom selected from element group (c) consisting of B, Al, Si, P, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, and As.

7. The nonaqueous electrolyte battery according to claim 6, wherein some of the heteroatoms in the heteropolyacid and the heteropolyacid compound are replaced with at least one element selected from the group consisting of H, Be, B, C, Na, Al, Si, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Zr, Rh, Sn, Sb, Te, I, Re, Pt, Bi, Ce, Th, U, and Np.

8. The nonaqueous electrolyte battery according to claim 1, wherein the at least one of a heteropolyacid and a heteropolyacid compound includes silicotungstic acid ( $H_4SiW_{12}O_{40}$ ).

9. The nonaqueous electrolyte battery according to claim 1, wherein the binder includes polyvinylidene fluoride.

10. A nonaqueous electrolyte battery comprising:

a positive electrode having a positive electrode active material layer that includes a positive electrode active material, a binder, and a compound having a pyrrolidone skeleton;



a negative electrode having a negative electrode active material layer;  
a nonaqueous electrolyte that includes a solvent and an electrolyte salt; and  
a coating that originates in at least one of a heteropolyacid 5  
and a heteropolyacid compound, and is formed on the positive electrode.

\* \* \* \* \*